SYNTHESIS AND CHARACTERIZATION OF
NANOSTRUCTURED ELECTRODES FOR
SOLID STATE IONIC DEVICES

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Presented to
The Academic Faculty

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SYNTHESIS AND CHARACTERIZATION OF
NANOSTRUCTURED ELECTRODES FOR
SOLID STATE IONIC DEVICES

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Yuelan Zhang

June, 2006, in Atlanta, GA, USA
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Significance of this Research</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Scope of Research and Objectives</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>Overview of the Upcoming Chapters</td>
<td>5</td>
</tr>
<tr>
<td>1.4</td>
<td>Reference</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>BACKGROUND</td>
<td>7</td>
</tr>
<tr>
<td>2.1</td>
<td>Solid Oxide Fuel Cells</td>
<td>7</td>
</tr>
<tr>
<td>2.1.1</td>
<td>Configuration of a Solid Oxide Fuel Cell</td>
<td>7</td>
</tr>
<tr>
<td>2.1.2</td>
<td>Thermodynamics</td>
<td>9</td>
</tr>
<tr>
<td>2.1.3</td>
<td>Electrode Polarization and Kinetics</td>
<td>9</td>
</tr>
<tr>
<td>2.1.4</td>
<td>Triple Phase Boundaries</td>
<td>16</td>
</tr>
<tr>
<td>2.1.5</td>
<td>Technical Challenges for SOFCs</td>
<td>18</td>
</tr>
<tr>
<td>2.2</td>
<td>Lithium Ion Batteries</td>
<td>22</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Configuration of a Lithium Ion Batteries</td>
<td>22</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Challenges for Electrode Materials</td>
<td>25</td>
</tr>
</tbody>
</table>
3 EXPERIMENTAL TECHNICS

3.1 Chemical Synthesis Methods

3.1.1 Sol-gel Process

3.1.2 Hydrothermal Process

3.1.3 Templating Method by Breath Figure Patterns

3.2 Characterization Techniques

3.2.1 Microstructural and Phase Characterization

3.2.1.1 Scanning Electron Microscopy

3.2.1.2 Transmission Electron Microscopy

3.2.1.3 X-ray Diffraction

3.2.1.4 BET Surface Area Analysis

3.2.2 Electrochemical Characterization

3.2.2.1 Gavanostatic Interrupt Titration Technique

3.2.2.2 Potential Step under Diffusion Control

3.2.2.3 Cyclic Voltammetry

3.2.2.4 Electrochemical Impedance Spectroscopy

3.3 References

4 NANOSTRUCTURED ELECTRODES FOR LITHIUM ION BATTERIES

4.1 Macroporous LiMn$_2$O$_4$ Positive Electrode for Lithium Ion Batteries

4.1.1 Introduction

4.1.2 Experimental

4.1.2.1 Preparation of Macroporous LiMn$_2$O$_4$ Powders

4.1.2.2 Characterization

4.1.3. Microscopic Properties and Crystallinity of LiMn$_2$O$_4$ Powder
4.1.4. Electrochemical Behavior of Macroporous LiMn$_2$O$_4$ Powders

4.1.4.1 Reversibility

4.1.4.2 Rate Capability

4.1.4.3 Cyclability

4.1.4.4 Electrode Kinetics

4.1.5 Conclusions

4.2 Nanostructured SnO$_2$ Negative Electrode for Lithium Ion Batteries

4.2.1 Introduction

4.2.2 Experimental

4.2.2.1 Preparation of SnO$_2$ thin film

4.2.2.2 Characterization of SnO$_2$ thin film

4.2.3 Microscopic Properties

4.2.4 Electrochemical Properties

4.2.4.1 Alloying Mechanism

4.2.4.2 Cycling Studies

4.2.4.3 Rate Capability

4.2.5 Conclusions

4.3 References

5 Nanostructured Cathode for Solid Oxide Fuel Cells

5.1 Synthesis of Multi-scale Porous MIEC Electrodes

5.1.1 Introduction

5.1.2 Experimental

5.1.2.1 Preparation of Multi-scale Porous MIEC film

5.1.2.1 Characterization Methods

5.1.3 Microscopic Features of Multi-scale Porous MIEC film
LIST OF TABLES

Table 2-1 Comparison of Cathode Materials 27

Table 4-1: Experiment conditions for glycine-nitrate combustion process 59

Table 4-2: Comparison of the capacities of various SnO2 thin films (unit: μAh/cm²-μm) 90
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>a) Comparison of conductivity profiles in the semi-infinite space-charge and mesoscale situations. The concentration or (parallel) conductivity profiles are sketched for the semi-infinite situation (period &gt;8(\lambda_D)), and for the mesoscale situation (period &lt;8(\lambda_D), right) in which the space-charge regions overlap and bulk values are exceeded even in the centers of the individual layers.(\lambda_D) is Debye length, which is about 10 nm, in view of extrinsic-intrinsic transition of the pure materials. b) Parallel ionic conductivity of the films. Data are shown for films with various periods and interfacial densities in the 430-16 nm range. The overall thickness is approximately the same in all cases.</td>
</tr>
<tr>
<td>2-1</td>
<td>Schematics of operating concept of a SOFC</td>
</tr>
<tr>
<td>2-2</td>
<td>Schematic of the effect of the discharge current on the cell voltage and power</td>
</tr>
<tr>
<td>2-3</td>
<td>Schematic of Knudsen diffusion</td>
</tr>
<tr>
<td>2-4</td>
<td>Schematic of Fickian Diffusion</td>
</tr>
<tr>
<td>2-5</td>
<td>Schematics of Triple Phase Boundaries</td>
</tr>
<tr>
<td>2-6</td>
<td>Schematic diagram of TPBs of a) a porous single-phase electronically conductive cathode. TPBs are located at the cathode/electrolyte interface; b) a single porous MIEC phase transfers both electrons and oxygen vacancies; and c) porous MIEC composite. TPBs are extended throughout the bulk.</td>
</tr>
<tr>
<td>2-7</td>
<td>Total cell resistance, cathode (Ag-Bi(<em>{2})V(</em>{0.9})Cu(<em>{0.1})O(</em>{5.35})) interfacial polarization resistances, and electrolyte (Gd(<em>{0.1})Ce(</em>{0.9})O(_{1.95})) resistances as a function of cell operating temperature</td>
</tr>
<tr>
<td>2-8</td>
<td>Schematics of a functionally graded cathode with (a) graded microstructure and (b) graded composition.</td>
</tr>
<tr>
<td>2-9</td>
<td>Schematic of a Lithium ion battery cell</td>
</tr>
<tr>
<td>2-10</td>
<td>Part of the unit cell of LiMn(_2)O(_4) showing the local structure around octahedrally coordinated manganese in an ideal spinel lattice. Mn-O bonds are represented by heavy solid lines; linear chains of Mn ions in neighboring edge-sharing octahedral are indicated by dashed lines.</td>
</tr>
</tbody>
</table>
Figure 2-11 a) The Li–Mn–O phase diagram, b) a close-up of the Li$_2$MnO$_3$ – LiMnO$_2$ – $\lambda$-MnO$_2$ part of the Li-Mn-O phase diagram

Figure 2-12 On the left, expanded view of the framework built on FeO$_6$ octahedral and PO$_4$ tetrahedral, with Li ions in red. The FeO$_6$ octahedral are linked together through corner sharing in the (b, c) plane. On the right, restricted view of Li, Fe and P distribution between two distorted, h.c.p. (hexagonal close packed) oxygen-dense layers (PTd[LiFe]oct.O4). LiO$_6$ octahedral share edges and Li ions may diffuse along [010] and [001].

Figure 3-1: Simplified Chart of sol-gel processes

Figure 3-2: Schematic of the general hydrolysis reaction scheme

Figure 3-3: Self-assembly 3D hexagonal porous polymer thin film prepared by breath figures

Figure 3-4: A model for the formation of the structure in polymer films. The images are color-coded, with blue and orange denoting low and high temperatures, respectively, relative to room temperature. (a) The conditions under which the experiment is performed. (b) Evaporation of the solvent cools the solution surface, thus initiating the nucleation and growth of moisture. (c) Because of the convective currents arising from the evaporation as well as from the airflow across the surface, the water droplets pack into a hexagonal array. (d to f) We hypothesize that the ordered array sinks into the solution, thus leaving the surface of the solution free for the nucleation and growth of moisture to form another ordered array of water droplets. (g) When all of the solvent has evaporated, the film must return to room temperature, thus allowing the water droplets to evaporate as well while leaving behind the scaffold.

Figure 3-5: Schematic of Diffraction of X-rays

Figure 3-6: Principles of the galvanostatic intermittent titration technique (GITT) for evaluation of kinetic data of electrode. A constant current is applied and interrupted after certain time intervals $\tau$ until an equilibrium cell voltage is reached. During the current pulses, the transient voltage $E_t$ is observed as a function of time $t$ and analyzed to evaluate the chemical diffusion coefficient $D$. The steady-state equilibrium voltage is studied as a function of the composition

Figure 3-7: Cyclic potential sweep

Figure 3-8: Schematic of cyclic voltammogram
Figure 4-1: SEM images of calcined LiMn$_2$O$_4$ powders at 800°C: (a-b) low and high magnification of SEM images of LiMn$_2$O$_4$ powders prepared under sample S1 condition; (c-d) low and high magnification of SEM images of LiMn$_2$O$_4$ powders prepared under sample S2 condition. (e-f) low and high magnification of SEM images of LiMn$_2$O$_4$ powders prepared under sample S3 condition; (g-h) low and high magnification of SEM images of LiMn$_2$O$_4$ powders prepared under sample S4 condition.

Figure 4-2: X-Ray diffractograms of as-synthesized and calcined LiMn$_2$O$_4$ powders at 800°C for 2hrs for sample S1

Figure 4-3: X-Ray diffractograms of as-synthesized and calcined LiMn$_2$O$_4$ powders at 500°C, 700°C and 800°C for 2hrs for sample S2

Figure 4-4: X-Ray diffractograms of as-synthesized and calcined LiMn$_2$O$_4$ powders at 800°C for 2hrs for sample S3

Figure 4-5: TEM images of (a) as-synthesized and (b) calcined powders

Figure 4-6: Typical cyclic voltammogram of calcined spinel LiMn$_2$O$_4$ powders

Figure 4-7: Galvanostatic charge/discharge curve at the current density of 49.0 μA/cm$^2$ (C/5 Rate).

Figure 4-8: (a) Dependence of voltage profile on applied current density and (b) variation of fractional discharging capacity retention in discharging rate (open circle), reconstructed from Fig. 4-8a. For the sake of comparison, the discharging capacity retention of the LiMn$_2$O$_4$ prepared by a conventional solid-state reaction was included (open square). The specific discharge capacities at C/4 rate of two samples prepared by GNP and solid-state reaction were 108 and 112 mAh/g, respectively

Figure 4-9: Dependence of discharging capacity retention of calcined powders on the number of cycles at the cycling rate of 122.4 μA/cm$^2$ (C/2)

Figure 4-10: Typical chronoamperometric curves of calcined powders

Figure 4-11: a) Typical voltage transient during a current application and a subsequent current interruption in the GITT experiment and cell voltage (V) vs. time$^{1/2}$ ($t^{1/2}$) plot in a very short time range (insert in (a)) showing the linear relationship between V and $t^{1/2}$, and (b) open circuit voltage obtained from the GITT experiment (open circle) and chemical diffusion coefficient (solid circle) as a function of lithium content

Figure 4-12: Schematic of the configuration of test cell

Figure 4-13: XRD pattern of as-prepared nanostructured tin oxide thin film
Figure 4-14: SEM images of nanostructured tin oxide thin film a) side view, and b) top view. Insets are enlarged images.

Figure 4-15: The first potential profiles vs. the capacity of nanostructured tin oxide thin film tested at a constant current density of 0.1 mA/cm².

Figure 4-16: Discharge capacities vs. the number of charge/discharge cycles for the nanostructured tin oxide thin film. The charge/discharge rate is 0.3 mA/cm².

Figure 4-17: Rates of lithium insertion and desertion (dQ/dV) as function of voltage for the nanostructured tin oxide thin film, a) during charge; and b) during discharge. The first, fifth, tenth and thirtieth cycles are shown.

Figure 4-18: a) Discharge capacities vs. charge/discharge rate for the nanostructured tin oxide thin film (continued after cycle test shown in Figure 4-16), b) Capacity retention as discharge current density.

Figure 5-1: Schematic diagram of TPBs of a porous cathode only providing electrons (TPBs are located at the cathode/electrolyte interface) (left), and MIEC cathode transfers both electrons and oxygen vacancies (TPBs are extended to the surface of the MIEC) (right).

Figure 5-2: Schematic of the electrode processing to form multi-scale porous electrodes. (a-b) A polymer film with uniform array of pores (“air bubbles”) could be formed by a moisture casting process: spreading a layer of dilute polymer solution in a volatile solvent on an electrolyte substrate and subsequent solvent evaporating under moisture. (c) Slurry coating of prepared MIEC nanocomposites and (d) burning off of the polymer film and binder.

Figure 5-3: SEM images of PMMA spheres prepared by surfactant-free emulsion polymerization. The particle sizes are a) 310 nm, b) 500nm, and c) 600 nm.

Figure 5-4: SEM images of (a) foamy PMMA film, (b) as prepared green structure of foamy PMMA after infiltrated with SSC-GDC slurry, and (c-d) porous SSC-GDC electrode materials after fired at 550°C for 5hrs (insert is the enlargement of the wall composed of MIEC nanoparticles).

Figure 5-5: Nitrogen adsorption-desorption isotherms for a porous GDC-SSC materials calcined in air at 800°C for 2 hours.

Figure 5-6: BJH pore size distribution for a porous GDC-SSC materials calcined in air at 800°C for 2 hours.

Figure 5-7: TGA curves for MIEC materials (30wt.% GDC+SSC) from polymer foam.
Figure 5-8: Microstructures (SEM photographs) of (a-b) interconnected porous SSC-GDC MIEC cathode fired at 800°C for 2hrs (insert shows the nanostructure of porous wall area); and (c) SSC-GDC MIEC cathode prepared by slurry coating without template.

Figure 5-9: X-ray diffraction patterns of composite cathode (SSC and 30wt.% GDC)

Figure 5-10: (a) Impedance spectra of a cell with configuration of SSC-GDC/(Bi$_2$O$_3$)$_{1.75}$(Y$_2$O$_3$)$_{0.25}$/Pt. (b-c) The cathodic polarization resistances, $R_p$, of the interface between porous GDC-SSC and a dense (Bi$_2$O$_3$)$_{1.75}$(Y$_2$O$_3$)$_{0.25}$ electrolyte as determined from impedance spectra acquired at different temperature

Figure 5-11: (a-b) SEM photograph of dual scale porous NiO-GDC anode film fired at 800°C for 2hrs (insert shows the nanostructure of porous wall in white block).

Figure 5-12: X-ray diffraction patterns of composite anode (NiO and 35 wt.% GDC)

Figure 5-13: Schematic of the electroding process on honeycomb electrolyte

Figure 5-14: A cross-sectional view (SEM) of a GDC-LSM composite cathode fired at 800°C for 4 hours

Figure 5-15: TEM image of the GDC-LSM composite cathode fired at 800°C for 4 hours

Figure 5-16: The XRD pattern of a composite GDC-LSM powder prepared with a sol-gel process and fired at 1000°C for 2 hours (the XRD patterns of LSM and GDC fabricated with a glycine-nitrate process and a sol-gel method, respectively, are also shown for comparison).

Figure 5-17: A typical impedance spectrum for a symmetric cell, GDC-LSM/YSZ/GDC-LSM, as measured at 700°C in air. The polarization resistance of the electrode (LSM-GDC) and the electrolyte (YSZ) interface, $R_p$, was determined directly from this impedance spectrum

Figure 5-18: Interfacial polarization resistances of LSM-GDC electrodes (on an YSZ electrolyte) prepared by different processes: a sol-gel process as reported in this work, a slurry coating, a spin coating, and a spray coating process.

Figure 6-1: (a) The standard XRD pattern of hexagonal Ce(OH)CO$_3$, (b) the as-grown cerium compounds with precursor ratio of Ce$^{4+}$ to H$_2$O at 1:20, (c) fired samples at 500°C for 5h
Figure 6-2: SEM images of as-grown cerium compounds with microflower shape under hydrothermal conditions at 180°C (molar ratio of Ce⁴⁺ to H₂O =1:20). (a)-(b) Ce(OH)CO₃ micro-flower at different magnifications, (c) top view of nanopetals, (d) side view of the nanopetals, (e) enlarged view of nanopetals without gold coating.

Figure 6-3: (a) TEM images of cerium compound nanopetals, (b) selected-area electron diffraction (SAED) pattern of the nanopetals in (a). The spot pattern is indexed as Ce(OH)CO₃ nanopetals. They have textured orientation along [0001]. The shaded ring pattern is indexed as ceria.

Figure 6-4: (a)-(b) SEM images of as-prepared ceria; (c) TEM image of as-prepared ceria in (a-b); (d) SAED pattern of as-prepared ceria in (c). The molar ratio of Ce⁴⁺ to H₂O is 1:100.

Figure 6-5: XRD patterns of the as-grown cerium compounds with the precursor ratio of Ce⁴⁺ to H₂O at (a)1:20, (b)1:40, (c) 1:100. (* stands for hexagonal Ce(OH)CO₃, and filled circles stand for CeO₂.)

Figure 6-6: Raman spectra of a CeO₂ microflower sample collected (after evacuation at 50°C) at room temperature sequentially in (a) Ar, (b) 10% O₂+Ar, (c) 10% CH₄+Ar, and (d) 10% O₂ +Ar.

Figure 6-7: Raman spectra characterizing O₂ adsorption (a) on CeO₂ microflowers with aggregated nanoparticles and (b) on CeO₂ nanoparticles, both of which had been exposed to 5% H₂ at 400°C and then exposed to 10% O₂.
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
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<tr>
<td>3DOM</td>
<td>Three-dimensionally ordered macroporous</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<td>BF</td>
<td>Breath Figure</td>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
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<tr>
<td>CCV</td>
<td>Close circuit voltage</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
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<td>GDC</td>
<td>Gadolinium doped ceria</td>
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<td>GNP</td>
<td>Glycine-nitrate process</td>
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<td>GITT</td>
<td>Galvanostatic intermittent titration technique</td>
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<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma - Mass Spectrometry</td>
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<td>IS</td>
<td>Impedance spectroscopy</td>
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<tr>
<td>LCT</td>
<td>Liquid crystal templating</td>
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<tr>
<td>LSM</td>
<td>Strontium doped lanthanum manganite</td>
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<tr>
<td>LSC</td>
<td>$La_{1-x}Sr_xCoO$</td>
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<td>LSCF</td>
<td>$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$</td>
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<tr>
<td>MIEC</td>
<td>Mixed ionic and electronic conductor</td>
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<td>OCV</td>
<td>Open circuit voltage</td>
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<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<td>SDC</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SOFC</td>
<td>Solid oxide fuel cell</td>
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<td>SSC</td>
<td>Sm$<em>{0.5}$Sr$</em>{0.5}$CoO$_3$</td>
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<td>SAED</td>
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# LIST OF SYMBOLS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
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</tr>
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<td>$\alpha$</td>
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<td>Number of electrons</td>
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<td>$N_A$</td>
<td>Avogadro’s number</td>
</tr>
</tbody>
</table>
$O_{ox}$  Kröger-Vink notation for Oxygen ions

$P_0$  Equilibrium Pressure

$P_i$  Partial pressure of component i

$P_s$  Saturation Pressure

$R$  Gas constant or Electrical resistance

$R_p$  Interfacial Polarization resistance

$Z_{Im}$  Imaginary part of impedance

$Z_{Re}$  Real part of impedance

$T$  Absolute Temperature

$t$  time

$V_{o}^{**}$  Kröger-Vink notation for Oxygen vacancy
SUMMARY

Solid-state electrochemical energy conversion and storage technologies such as fuel cells and lithium ion batteries will influence the way we use energy and the environment we live in. The demands for advanced power sources with high energy efficiency, minimum environmental impact, and low cost have been the impetus for the development of a new generation of batteries and fuel cells. Currently, lithium ion battery technology’s greatest disadvantages are long-term cycling stability and high charge/discharge rate capabilities. On the other hand, fuel cell technology’s greatest disadvantage is cost. It is found that these problems could be attenuated by the incorporation of nano-structured materials. But, we are still far away from possessing a solid scientific understanding of what goes on at the nanoscale inside these solid state ionic devices, and what is the relationship between nano-structures and their electrochemical properties, especially between the microstructure and electrode polarization and degradation. Electrode polarization represents a voltage loss in an electrochemical energy conversion process. Such understanding is critical for further progress in solid state ionic devices.

This thesis focused on the design, fabrication, and characterization of nano-structured porous electrodes with desired composition and microstructure to minimize electrode polarization losses in the application of fuel cells and lithium ion batteries. Various chemical methods such as sol-gel, hydrothermal, surfactant, colloidal and polymer template-assisted processes have been applied in this work. And various
characterization techniques have been used to explore the understanding of the microscopic features with electrochemical interfacial properties of the electrodes.

Solid-state diffusion often limits the utilization and rate capability of electrode materials in a lithium-ion battery, especially at high charge/discharge rates. When the fluxes of \( \text{Li}^+ \) insertion or extraction exceeds the diffusion-limited rate of \( \text{Li}^+ \) transport within the bulk phase of an electrode, concentration polarization occurs. Further, large volume changes associated with \( \text{Li}^+ \) insertion or extraction could induce stresses in bulk electrodes, potentially leading to mechanical failure. Porous electrodes with high surface-to-volume ratio would increase the electrochemical reaction surface and suppress the mechanical stress. But porous electrodes also increase the tortuosity of mass transport within solid electrodes. Interconnected porous materials would decrease the percolation threshold for porous electrodes. In this work, electrodes with unique architecture for lithium ion batteries have been fabricated to improve the cycleability, rate capability and capacity retention. Spinel \( \text{LiMn}_2\text{O}_4 \) with interconnected macropores was created using a glycine-nitrate combustion process. Both microstructure and phase crystallinity were optimized by adjusting the fuel/oxidant ratio. This macroporous \( \text{LiMn}_2\text{O}_4 \) positive electrode exhibited better capacity retention and rate capability than those with larger particle size prepared by solid state reaction. Detailed electrode kinetic studies indicated that the macroporous microstructure promoted lithium diffusion and the overall reaction process was not controlled by lithium diffusion. Nanostructured tin oxide thin films with columnar grains less than 20 nm were deposited on Au/Si substrate using a combustion CVD method. The microstructure was highly porous and open, and thus was easily accessible to liquid electrolyte. In addition, the microstructure with vertical and radial
connectivity of active materials led to decreased tortuosity for mass transport within solid electrodes. Nanoparticles accommodated the large volume change during cycling. These thin film electrodes exhibited highly reversible specific capacity and good capacity retention. It is about 93% after 80 cycles at a charge/discharge rate of 0.3 mA/cm². When discharged at 0.9 mA/cm², the obtained capacity retention was about 64% of the capacity at 0.3 mA/cm².

Cathodic interfacial polarization represents the predominant loss in a low-temperature SOFC. In this thesis, several porous nanocomposite electrodes of mixed ionic and electronic conductors (MIEC) with high surface areas were designed and fabricated to improve to minimize the polarization resistance. For the first time, regular, homogeneous and dual porous MIEC electrodes were successfully fabricated using breath figure templating, which is self-assembly of the water droplets in polymer solution. The homogeneous macropores promoted rapid mass transport by decreasing the tortuosity. Further, mesoporous microstructure provided more surface areas for gas adsorption and more TPBs for the electrochemical reactions. The interfacial polarization resistances were 0.94 and 0.39 $\Omega$cm² at 700 and 750°C, respectively. Furthermore, electrodes consisting of strontium doped lanthanum manganite (LSM) and gadolinium doped ceria (GDC) were developed with a modified sol-gel process for honeycomb SOFCs based on stabilized zirconia electrolytes. The sol gel derived cathodes with fine grain size and large specific surface area, showed much lower interfacial polarization resistances than those prepared by other processing methods. And this process developed strong bonding between the electrode and electrolyte even at low temperatures. The interfacial polarization resistances were 0.65 and 0.16 $\Omega$cm² at 650 and 750°C, respectively. The
mesoscopic regime of overlapping space charge effects had a positive effect on the electrode kinetics.

Ceria is a very important catalytic material for fuel reforming in SOFCs and CO poisoning in PEM fuel cells. Especially, the design of a new generation SOFC requires the in-situ reforming of hydrocarbon fuels. In this work, nanostructured ceria was developed via a controlled hydrothermal process in a mixed water-ethanol medium. The microstructure, formation mechanism, and their surface catalytic properties were investigated.
CHAPTER 1

INTRODUCTION

1.1 Significance of this Research

The current energy supply system, which is based on the combustion of fossil fuels, causes many environmental problems: air pollution, acidifying emissions, and the emission of greenhouse gases. Such problems and the emerging energy crisis pose the question of how to use energy in the earth more efficiently while keeping our living space clean. Solid-state ionic devices, such as SOFCs, lithium ion batteries and solar cells, are promising energy conversion and storage technologies that could solve some environmental issues, while simultaneously curbing the possible exhaustion of resources and providing employment opportunities.

The solid oxide fuel cell is currently attracting tremendous interest because of its huge potential for power generation in stationary, portable and transport applications and of the increasing need for sustainable energy resources. The major current impediment of commercializing SOFCs is cost which results from high operating temperature. There is considerable interest in lowering the operating temperature, in particular, to reduce the cost of interconnect, manifolding and sealing materials, as well to preclude the potential problem resulting from the sintering of electrode particles over time.\textsuperscript{[1]} Although significant advances have been achieved in the development of materials with improved ionic and electronic conductivity and of manufacturing processes to fabricate thinner electrolytes to reduce ohmic losses, the performance at lower temperature is severely limited by interfacial polarization resistance at the cathode/electrolyte interfaces. The main problem lies with the development of sufficiently active cathode materials. Design
and fabrication of functional, porous, nanostructured electrode to maximize the area of the three-phase boundary (TPB) between ionic, electronic conductor and oxygen gas, remain at the forefront of fuel cell research and development.

With the rapid advancement in miniaturization of microelectronic and telecommunication devices, the portability and reliability of these devices is limited by available battery systems. The key to the successful development of a new generation of lithium batteries depends critically on the creation of new electrodes and electrolyte materials with composition and configuration that offer high power density, long shelf and cycle life, low cost, and minimal disposal problems. One of the major challenges facing the development of novel lithium ion rechargeable batteries is the development of high performance electrode materials with excellent cycleability (cycle life) and minimal capacity fade.

Therefore, new designs of architecture and fabrication processes are desirable in order to create durable, effective, and porous structures for electrodes. This work aims to design and synthesis of nanostructured MIEC (mixed ionic and electronic conductor) electrode architecture based on the 3D interconnected pores. MIEC can simultaneously transport both ionic and electronic defects. Porous MIEC as electrodes can dramatically increase the active reaction sites, i.e., TPBs, which greatly influence the performance of the electrodes. Nanostructured materials are distinguished from conventional polycrystalline materials by the size of the structural units that compose them.\textsuperscript{[2]} Further they often exhibit drastically different properties from polycrystalline materials, especially in interface modification.\textsuperscript{[3]} As shown in Figure 1-1, when the thickness of the ionic conductor films decrease to some degree, at which the semi-infinite diffusion is no
longer valid and finite diffusion takes effect, the ionic conductivity is enhanced dramatically in the space charge zone. Thus the 3-Dimensional open configurations have a significant advantage of having short diffusion distances which provide enough active surfaces.

Figure 1-1 a) Comparison of conductivity profiles in the semi-infinite space-charge and mesoscale situations. The concentration or (parallel) conductivity profiles are sketched for the semi-infinite situation (period >8λD), and for the mesoscale situation (period <8λD, right) in which the space-charge regions overlap and bulk values are exceeded even in the centers of the individual layers. λD is Debye length, which is about 10 nm, in view of extrinsic-intrinsic transition of the pure materials. b) Parallel ionic conductivity of the films. Data are shown for films with various periods and interfacial densities in the 430-16nm range. The overall thickness is approximately the same in all cases. [3]
1.2 Scope of Research and Objectives

While various fabrication techniques have been studied, an effective approach to fabricate electrodes with the desired composition and microstructure at a reasonable cost is still lacking. And due to the fact that electrode processes and morphology are closely related, and also that the fundamental mechanisms are not fully understood, a consistency of the relationship between the microstructure and their performance is still lacking.

The overall objective of this work is to develop and characterize functionally nanostructured electrode materials with high surface area for electrochemical and catalytic applications. Nanostructured materials are fabricated via the chemical synthesis methods such as combustion method, sol-gel, hydrothermal process and template assisted process. In order to obtain macroscopic ordered structure, the templated self-assembly are employed. The quantitative and qualitative characterization of electrode microstructure, and analysis of correlation between microstructure and their properties in electrochemical catalytic or intercalation application are investigated.

To be more specific, the objectives of this research are:

1. To optimize the processes for preparation of nanostructured tin oxide and lithium manganese oxide that will serve as electrodes for lithium ion batteries, and to characterize microstructure and cycleability of the prepared samples via TEM, BET, CV chronoamperometry and galvanostatic techniques respectively;

2. To synthesize interconnected multi-scale porous MIEC electrodes by breath figure templating, and to characterize their microscopic features and electrochemical properties by SEM, BET and EIS;
3. To develop a new sol-gel derived process to fabricate ultra-fine MIEC nanoparticle, and to characterize their microscopic features and electrochemical properties by SEM, TEM, BET and EIS;

4. To develop nanostructured cerium oxide by hydrothermal process, and to characterize their surface catalytic properties to hydrocarbon fuel and CO oxidation by Raman.

1.3 Overview of the Upcoming Chapters

The thesis begins with the introductory chapter that introduces the ideas compelling the research conducted and outlines the research work undertaken to achieve the goal. Chapter 2 gives a general review of the SOFCs and lithium ion batteries, including their configuration, operation mechanism, kinetics influencing the electrode polarization and the curbing issues, as well as porous electrodes. Synthesis and characterization technique methods employed in the thesis are described in Chapter 3. Chapter 4 presents the synthesized nanostructrued electrodes for lithium ion batteries, including macroporous spinel LiMn$_2$O$_4$ positive electrode and nano-columnar SnO$_2$ thin film negative electrode. Chapter 5 presents the porous cathode for SOFCs, including multi-scale porous cathode prepared by a novel method and a sol-gel derived method. Chapter 6 presents cerium oxide with a novel microstructure and its surface properties. The mechanism and related electrochemical and catalytic properties are investigated and discussed in detail. The conclusion and recommendation are given in the final chapter.

1.4 Reference


CHAPTER 2

BACKGROUND

Energy consumption/production that relies on the combustion of fossil fuel is forecast to have a severe future impact on world economics and ecology. Electrochemical energy production is under serious consideration as an alternative energy/power source. Systems for electrochemical energy storage and conversion include batteries, fuel cells and electrochemical capacitors. Although the energy storage and conversion mechanisms are different, there are electrochemical similarities of these systems. Common features are that the energy-providing processes take place at the phase boundary of the electrode/electrolyte interface and that charge (electron and ion) transport are separated.

2.1 Solid Oxide Fuel Cells

A solid oxide fuel cell (SOFC) is an all-solid-state energy conversion device that converts the chemical energy of a fuel (including hydrogen, natural gas, coal-derived synthetic gas, reformed gasoline or diesel) into electrical energy by electrochemically combining fuel and oxidant gases across an ionic conducting ceramic without combustion. The SOFC is simple, highly efficient (~85% in theory) compared to engines and modern thermal power plants (~30%), reduced environmental impact, and can at least partially internally reform hydrocarbon fuels. It is clean, reliable, and almost entirely nonpolluting.

2.1.1 Configuration of a SOFC

The core components of a single cell are electrolyte, anode and cathode. An electrolyte is a material that provides pure ionic conductivity between the positive and
negative electrode of a cell. The anode is the negative electrode of a cell associated with oxidative chemical reactions that release electrons into the external circuit. The cathode is the positive electrode of a cell associated with reductive chemical reactions that gain electrons from the external circuit.

Figure 2-1 shows an SOFC operating scheme. It contains a solid oxide electrolyte made from ceramic such as yttria-stabilized zirconia (YSZ) which acts as a conductor of oxide ions at temperatures from 600 to 1000°C. This ceramic material allows oxygen atoms to be reduced on its porous cathode surface by electrons, thus being converted into oxide ions, which are then transported through the ceramic hydrogen, giving up electrons to an external circuit as shown in Figure 2-1.

Figure 2-1. Schematics of operating concept of a SOFC [3]
2.1.2 Thermodynamics \([1,4,5]\)

The overall reaction in an SOFC is the oxidation of \(H_2\) to form \(H_2O\), namely,
\[
H_2\text{(gas, anode)} + \frac{1}{2}O_2\text{(gas, cathode)} \rightarrow H_2O\text{(gas, anode)}, \quad (2-1)
\]

The half cell reaction at the cathode is:
\[
\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \quad (2-2)
\]

And the half cell reaction at the anode is:
\[
H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (2-3)
\]

Under open circuit conditions, with electrochemical potential of oxide ions equilibrated across the oxide-ion conducting electrolyte, a voltage difference, \(E\), the Nernst potential, appears between anode and the cathode. It is related to the net free energy change of the reaction, \(\Delta G\), via the following reaction.
\[
\Delta G = -nFE = -2FE \quad (2-4)
\]

where \(n\) denotes the number of electrons participating in the reaction. The Nernst potential, \(E\), is the open circuit voltage, OCV, and is given by
\[
E_{OCV} = -\frac{\Delta G}{2F} = \frac{\Delta G^0}{2F} - \frac{RT}{2F} \ln \left( \frac{P_{H,O}^a}{P_{O_2}^{c1/2} P_{H_2}^a} \right) = E^0 + \frac{RT}{4F} \ln \left( \frac{P_{O_2}^c P_{H_2}^a}{P_{H,O}^a} \right) \quad (2-5)
\]

where \(P_{O_2}\) is the partial pressure of oxygen in the cathode gas, \(P_{H_2}\) and \(P_{H_2O}\) are respectively the partial pressure of \(H_2\) and \(H_2O\) in the anode gas, \(R\) is the gas constant, \(F\) the Faraday constant, and \(T\) the absolute temperature.

2.1.3 Electrode Polarization and Kinetics \([4,5,6]\)
Thermodynamics describe reactions at equilibrium and the maximum energy release for a given reaction. Compared to the equilibrium voltage (open circuit voltage), the voltage drops off when current is drawn from the cell because of kinetic limitations of reactions and of other processes must occur to produce current flow during operation.

Electrochemical reaction kinetics follows the same general considerations as those for bulk chemical reactions. However, electrode kinetics differs from chemical kinetics in the influence of the potential drop in the electrical double layer at an electrode interface as it directly affects the activated complex. The detailed mechanism of electrode reactions often involves a series of physical, chemical, and electrochemical steps, including charge-transfer and charge transport reactions. The rates of these individual steps determine the kinetics of the electrode of the cell.

Polarization is a voltage loss or overpotential, which is a function of current density. Basically, three different kinetics effects for polarization have to be considered (as shown in Figure 2-2): (1) activation polarization is related to kinetics of the electrochemical redox (or charge-transfer) reactions taking place at the electrode/electrolyte interfaces of anode and cathode; (2) ohmic polarization is interconnected to the resistance of individual cell components and the resistance due to contact problems between the cell and components; (3) concentration polarization is due to mass transport limitations during cell operation.

The polarization, $\eta$, is given by

$$\eta = E_{OCV} - E_{CCV} \quad (2-6)$$

where $E_{OCV}$ is the voltage of the cell at open circuit and $E_{CCV}$ is the close-circuit voltage, which is the terminal cell voltage with current flowing.
It is assumed that partial pressures of the various species are fixed just outside the electrodes, regardless of the local current density. Hence, the Nernst voltage, $E$, is not a function of current density.

![Diagram of cell voltage and power vs. current](image)

**Figure 2-2** Schematic of the effect of the discharge current on the cell voltage and power.[7]

2.1.3.1 Activation Polarization

Electrode reactions involve charge (electron) transfer as a fundamental step. Activation polarization arises from kinetics hindrances of the charge-transfer reaction taking place at the electrode/electrolyte interface. This type of kinetics is best understood using reaction rate theory. The rate, current flow, $I$ ($i=I/A$ and $i_0=I_0/A$, where $A$ is the
electrode surface area), of a charge-transfer-controlled electrochemical reaction can be given by the Bulter-Volmer equation as:

$$i = i_0 \exp(-\alpha \cdot F \cdot \eta / RT) - \exp[(1 - \alpha) / F \eta] / RT$$  \hspace{1cm} (2-7)

where $\alpha$ is the transfer coefficient, and the exchange current density $i_0$ equals to

$$i_0 = k^0 FA$$  \hspace{1cm} (2-8)

in which $k^0$ is the standard rate constant.

The activation polarization follows the Tafel equation derived from Equation (2-7)

$$\eta = a + b \log(i / i_0)$$  \hspace{1cm} (2-8)

Where $a$ and $b$ are constants.

Reactions with larger $i_0$ are more reversible and have lower polarization for given current flow. The buildup and decay of the activation polarization are fast and can be identified by the voltage change on current interruption in a time frame of $10^{-2} \sim 10^{-4}$ s.

In SOFCs, the oxygen reduction reaction is a multi-step process, usually comprising several parallel reaction pathways. A thorough understanding of the elementary processes in SOFC cathodes under realistic operating conditions has eluded researchers because of such multiplicity of pathways. Thus, despite numerous proposed reaction mechanisms for oxygen reduction, it is virtually impossible to select any one over another as definitive. This is also due to the fact that the reduction mechanisms are surely material and microstructure-dependent.

2.1.3.2 Ohmic Polarization
Ohmic polarization arises from the resistance of the electrolyte, electrode materials, current collectors, terminals and contact between particles to the motion of electrical charge. This behavior, in the simplest case, can be described by Ohm’s law.

\[ \eta = IR \]  

(2-9)

Ohmic polarization appears and disappears instantaneously \((\leq 10^{-6} \text{ s})\) when current flows and ceases.

2.1.3.3 Concentration Polarization

As the redox reactions proceed, the availability of the active species at electrode/electrolyte interface changes. Concentration polarization arises from limited mass transport capabilities, for example, limited diffusion of active species to and from the electrode surface to replace the reacted material to sustain the reaction. Diffusion limitations are relatively slow, and the buildup and decay take more than \(10^2\) s to appear.

For limited diffusion, the concentration polarization can be expressed as:

\[ \eta = \frac{RT}{nF} \ln\left(\frac{C}{C_0}\right) \]  

(2-10)

Where \(C\) is the concentration at the electrode surface and \(C_0\) is the concentration in the bulk. Porous electrode structures are used to extend the available surface area and lower the current density for more efficient operation.

In SOFCs, the reacting species are gaseous: at the anode \(\text{H}_2\) and at the cathode \(\text{O}_2\). At the anode, \(\text{H}_2\) must be transported through porous anode to the anode/electrolyte interface. Hydrogen then reacts with oxide ions transported through the electrolyte, at or near the anode/electrolyte interface, to form water and release electrons to the anode, for their subsequent transport to the cathode through the external circuit. The \(\text{H}_2\text{O}\) formed
must be transported away from the electrolyte/anode interface, through the porous anode to the fuel system.

Transport of gaseous species usually occurs by binary diffusion, where the effective binary diffusivity is a function of the fundamental binary diffusivity $D_{H_2O}$, and microstructural parameters of the anode. The anodic concentration polarization is a function of several parameters as follows:

$$\eta_{\text{conc}}^a = f(D_{H_2O}, \text{Microstructure}, \text{Partial pressure}, \text{Current density}) \quad (2-11)$$

It is assumed here that the effects of Knudsen diffusion, adsorption/desorption and surface diffusion are negligible. The concentration polarization increases with increasing current density due to the limitation of the mass transport to maintain the amount of current passing through the electrodes. The higher the diffusivity and partial pressure of the fuel, the higher the anode-limiting current density, and the lower the concentration polarization. From the standpoint of microstructural parameters, the lower the volume fraction porosity, the less electrochemical reaction sites; and the higher the tortuosity factor, the higher the concentration polarization.

Likewise, Concentration polarization at the cathode similarly is related to the transport of O$_2$ and N$_2$ through the porous cathode. And it can be described as follows:

$$\eta_{\text{conc}}^c = f(D_{O_2-N_2}, \text{Microstructure}, \text{Partial pressure}, \text{Current density}) \quad (2-12)$$

The tortuosity factor is a measure of the tortuous nature of the electrode through which diffusion must occur. In very fine microstructures, the tortuosity as a phenomenological parameter may include effects of Knudsen diffusion, surface diffusion, and possible effects of adsorption/desorption. The several types of transport in small pores are described as follows.
2.1.3.4 Transport in Small Pores

Knudsen Diffusion

Knudsen Diffusion [8] is described by the Einstein relation as follows:

\[ D_s(c) = \lim_{t \to \infty} \frac{1}{6Nt} \left( \sum_{i=1}^{N} \left| r_i(t) - r_i(0) \right|^2 \right) \]

(2-13)

where \( D_s \) is the self-diffusion coefficient, which depends on the concentration \( c \), \( t \) is time, \( N \) is the total number of particles in the system, and \( r_i \) is the position vector of particle \( i \).

Knudsen diffusion occurs when the mean free path is relatively long compared to the pore size, so the molecules collide frequently with the pore wall. Knudsen diffusion is dominant for pores that range in diameter between 2 and 50 nm.

![Figure 2-3 Schematic of Knudsen diffusion][9]

Molecular or Fickian Diffusion

Molecular, or transport, diffusion [10] occurs when the mean free path is relatively short compared to the pore size, and is described by Fick's law as follows:

\[ J = -D_t \nabla c \]

(2-12)

where \( J \) is the mass flux, \( D_t \) is the transport diffusion coefficient (or Fickian diffusion coefficient), and \( \nabla C \) is the concentration gradient. The transport diffusivity relates the macroscopic flux of molecules in a system to a driving force in the concentration. This
diffusion mode is applicable to Brownian motion, where the movement of each particle is random and not dependent on its previous motion.

Transition Diffusion

Transition-mode diffusion has properties of both Knudsen and Fickian diffusion. A dynamic Monte Carlo simulation \[^{[11]}\] predicted that the trapping zone of the pore leads to a decrease in self-diffusivity but does not affect transport diffusivity.

Surface Diffusion

Surface diffusion\[^{[12]}\] is also used to explain a type of pore diffusion in which solutes adsorb on the surface of the pore and hop from one site to another through interactions between the surface and molecules. The surface diffusion is a very important phenomena and diffusion type at low temperature compared to grain boundary diffusion and bulk diffusion.

2.1.4 Triple Phase Boundaries \[^{[1, 5, 13]}\]

As illustrate in Figure 2-5, at the surface of the cathode of a SOFC, oxygen reduction can be described as follows:

\[
\frac{1}{2}O_2 + V_o^{**} + 2e' = O_o^x. \quad (2-13)
\]

where \(V_o^{**}\) is the oxygen vacancy and \(O_o^x\) is the oxygen ion.
Since this reaction involves ions, electrons, and gas molecules in three separate phases, the reaction site is often described as the three-phase (or triple-phase) boundary (TPB).

Figure 2-5 Schematics of Triple Phase Boundaries.

Thus, the reduction of oxygen takes place only at or near the TPBs the electrons are present simultaneously. The TPBs will remain electrochemically active only if electrons, oxygen vacancies, and oxygen ions can transport to and away from the TPBs. Mixed ionic and electronic conductors (MIECs) can simultaneously transport ionic and electronic defects. They can be a single phase (Figure 2-6b) or a composite (Figure 2-6c) composed of two phases.

Shown in Figure 2-6a [13] is the traditional porous cathode made of electronic conductors. TPBs exist at or near the electrolyte and electrode interface. By using porous MIECs as cathode, the electrochemically active reaction sites, i.e. TPBs could be extended to the entire MIEC/gas interface, which can be orders of magnitude larger than that of dense electrode or porous cathode only with electronic conductivity. The degree of this extension depends critically on the rate of defect transport through the solid MIEC, gas transport through the pores to promote surface coverage in the MIEC, and the catalytic activity of interfaces.
2.1.5 Technical Challenges for SOFCs

In spite of many advantages over the traditional combustion energy system, the commercialization of SOFCs is inhibited by the high costs associated with the high operating temperature. To compete commercially with conventional power generation, the operating temperature of SOFC systems must be lowered to reduce the fabrication
and material cost. If the operating temperature of SOFCs can be reduced to 400~600°C while maintaining a desirable performance, the interconnect, heat exchangers, and structure components could be fabricated from relative inexpensive components. Furthermore, lower operating temperatures would also resolve other technical issues such as materials compatibility, microstructure stability and thermal expansion compatibility.

However, while lowering the operating temperature lowers system cost, it also lowers cell performance. As shown in Figure 2-7[14], the interfacial polarization resistances increase dramatically as the operating temperature of a SOFC is reduced. Thus, the key technical challenge is how to minimize electrode polarization losses especially at the cathode/electrolyte at low operation temperatures. The most effective way to minimize polarization resistance is to use nanostructured porous interconnected mixing ionic and electronic conductors (MIECs) with functionally graded compositions or graded microstructures.

![Figure 2-7](image)

Figure 2-7. Total cell resistance, cathode (Ag-Bi₂V₀.₉Cu₀.₁O₅.₃₅) interfacial polarization resistances, and electrolyte (Gd₀.₁Ce₀.₉O₁.₉₅) resistances as a function of cell operating temperature.
Many fundamental issues regarding detailed electrode kinetics and transport mechanisms of defects and gas through the electrode systems remain unresolved.\cite{5, 15-16}

The performance of a porous MIEC electrode depends greatly on the transport of ionic and electronic defects in the solid phase, gas transport through the pores, and the electrochemical reactions occurring at the interfaces. Hence, there are two possible ways to minimize the interfacial polarization resistances and increase the kinetics of electrode reactions in SOFCs: 1) new materials with better intrinsic transport and catalytic properties, and 2) properly design and development of the architecture of the MIEC electrodes, including configuration of pores, connectivity of the porous micrstructure, graded composition and microstructure. Tailoring the microstructure of the composite electrode in terms of the relative particle size as well as the volume ratio of the components is important in controlling the TPB length as well as the continuity of the charge conduction pathways. Investigations on either exploring new materials with higher ionic or electronic conductivity or on fabrication of novel microstructure have been carried out accordingly.

Cathode materials for traditional SOFCs based on an yttria-stabilized zirconia (YSZ) electrolyte are MIEC composites consisting of strontium-doped lanthanum mangnites (LSMs) and YSZ. Usually, the operating temperature is above 800 °C. An alternative to YSZ is gadolinia-doped ceria (GDC), which has much higher conductivity than YSZ at reduced temperature region 600-800°C. The polarization resistance of an LSM-GDC cathode is 0.49 \(\Omega\text{cm}^2\) at 750°C, which is about three times less than that of an YSZ-LSM cathode on an YSZ electrolyte with similar microstructures.\cite{17} Moreover,
La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) and Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ (SSC), which are MIECs with considerable ionic conductivities, are used to replace LSM, a poor ionic conductor. The polarization resistance between an LSCF-GDC cathode and a GDC electrolyte are 0.2 $\Omega$cm$^2$ at 600°C.[18] A polarization resistance of 0.18 $\Omega$cm$^2$ at 600°C was achieved between an SSC-SDC (samaria-doped ceria) cathode and a SDC electrolyte.[19] At 500°C, the resistance of both system increased dramatically, from 0.2 $\Omega$cm$^2$ at 600°C to about 10 $\Omega$cm$^2$ at 500°C for an LSCF-GDC cathode,[18] and from 0.18 $\Omega$cm$^2$ to about 1 $\Omega$cm$^2$ for an SSC-SDC cathode.[19] Bismuth oxides have showed favorable catalytic effects on the oxygen disassociation reaction and exhibit conductivities with about 2 orders of magnitude higher than those of stabilized zirconia. Recently, interfacial resistances as low as 0.3 $\Omega$cm$^2$ at 600°C on an YSZ electrolyte, and 0.53 $\Omega$cm$^2$ at 500°C on a GDC electrolyte were reported.

Microstructure of MIECs plays a vital role in electrode performance. For example, the interfacial polarization resistance was 0.65 $\Omega$cm$^2$ at 650°C between a GDC-LSM cathode and YSZ electrolyte, which was decreased by more than 10 times for the same materials by varying particle/pore size, size distribution, porosity, MIEC configuration, etc. The normalized polarization resistance was obtained by timing nominal electrode area with experimental determined impedance. To improve the performance, design with functionally graded materials (FGM) which shows grade in composition (Figure 2-8a) or in morphology (Figure 2-8b) or both are introduced to the cathode[20]. The closest layer to electrolyte serves as electro-catalytically active layer and the outer layer serves as current collector. Based on design in Figure 2-8b, functionally
graded cathodes with LSM, YSZ and LSC displayed polarization resistance of 0.2 $\Omega \text{cm}^2$ at 750°C.\cite{20-21} It is encouraging for developing high power density SOFCs.

![Figure 2-8. Schematics of a functionally graded cathode with (a) graded microstructure and (b) graded composition.](image)

### 2.2 Lithium Batteries

Batteries are self-contained units that store chemical energy and, on demand, convert it directly into electrical energy to power a variety of applications. Batteries are divided into three general classes: primary batteries that are discharged once and discarded; secondary, rechargeable batteries that can be discharged and then restored to their original condition by reversing the current flow through the cell; and specialty batteries that are designed to fulfill a specific purpose. Lithium ion batteries are a type of rechargeable battery commonly used in consumer electronics. They are currently one of the most popular types of battery, with one of the best energy-to-weight ratios, no memory effect and a slow loss of charge when not in use.
2.2.1 Configuration of Lithium ion Battery

The new generation of ambient-temperature, nonaqueous, rechargeable lithium cell was invented in 1990. Figure 2-9 depicts the basic elements of a lithium ion battery and illustrates the operation of a lithium ion battery. A Li\(^+\) ion transfer cell is made using two different intercalation compounds as the electrodes in which the chemical potential of the intercalant differ by several electron volts. The negative electrode is a good reducing agent (electron donor). The positive electrode is an electron acceptor. The electrolyte is a pure ionic conductor that conducts lithium ions. The separator physically separates the anode from the cathode.
In Li\(^+\) ion transfer cells both electrodes are capable of reversible lithium insertion. The basic electrochemistry involves only the transfer of Li\(^+\) cations between the two insertion electrodes. The electrochemical insertion (electroinsertion) reactions are intrinsically simple and reversible. Because of the difference in chemical potentials of lithium in the two electrodes, the transfer of lithium ions from the negative electrode through the electrolyte into the positive electrode (discharge) deliver energy, whereas the reverse lithium transfer (charge) requires energy. The reaction at the negative electrodes usually proceeds as shown in Equation (2-14) \(^{[24]}\)

\[
Li_x M \leftrightarrow xLi^+ + xe^- + M \tag{2-14}
\]

Among the matrix metals, M, that form Li alloys electrochemically, for example, Al, Si, Sn, Bi, Ag have been studied most carefully \(^{[24]}\). Their specific charges are based upon the Li stoichiometric content in Li-metal alloys. Generally, the matrix metals undergo major structural changes when alloying with lithium.

The reaction at the positive electrodes is usually described as shown in Equation (2-15). Their specific charges are based on a reversible range \(\Delta x\) of the lithium content during the charging/discharging process \(^{[24]}\).

\[
\Delta x Li^+ + \Delta e^- + Li_x MO \xrightleftharpoons[charge]{dicharg} \rightarrow Li_{x+\Delta x} MO \tag{2-15}
\]

In general, the concepts of the thermodynamics and kinetics for lithium ion batteries are similar with those for SOFCs and hence they could be consulted in SOFC section.

The parameters that describe the performance of the lithium ion batteries include specific capacity, cycleability and rate capability.
*Specific capacity* expresses the total amount of electrical charge per unit weight or volume that a battery is able to hold.

The *rated capacity* is the total charge that a battery is able to deliver on discharge under some specific conditions (current density). The *rate capability* (rated capacity) of the charge/discharge reaction depends on the speed of transport of guests in the solid host. Decrease in grain size and diffusion path and increasing surface-to-volume ratio would improve rate capability. C-rate is a charge or discharge current rate of a battery expressed in amperes. It is a numerically a fraction or a multiple of the rated capacity of the battery expressed in ampere-hours. For example: for a 5-Ah rated capacity battery, C-rate is 5 A; C/5-rate is 1 A; 2C-rate is 10 A; and so on.

The *cycleability* (cycle life) expresses the number of times a rechargeable battery can be charged and discharged before it loses its ability to accept charge. The cycle life of Li+ ion transfer cells depends mainly on the dimensional stability of the host material during insertion and deinsertion of Li+.

### 2.2.2 Electrode Materials and Their Challenges

Some of the most attractive anode materials are tin-based oxide materials. Lithium first reacts irreversibly with tin-based oxide to form nanosized Sn domains, and then Sn is alloyed with Li and forms different Li-Sn alloys. Tin-based anode materials have shown promise of substantially exceeding carbon in lithium storage capacity. The charge storage capacity is up to 990 mAh/g, much larger than that of graphite (about 370 mAh/g); however, there is a significant irreversible capacity loss in the first cycle due to the *in situ* electrochemical reduction of tin oxide domains by lithium and a drastic expansion and contraction during charge and discharge. Moreover, the formed Li-Sn
alloy is very brittle, resulting in pulverization of the alloy and fast fading of capacity. All of these capacity losses are still major barriers to the successful application of lithium-metal alloys as anodes in lithium ion rechargeable batteries. Although a reduction in alloy particle size clearly benefits the cycleability by increasing tolerance to stress cracking, so far the gains are not sufficient.\[25\] However, it became clear that any physical or chemical means of overcoming the problem of reactant expansion should be beneficial, hence the use of composite negative electrodes. The basis behind this concept is the use of a ‘buffer matrix’ to compensate for the expansion of the reactants, so preserving the electrical pathway\[26\].

Economically and ecologically, LiMn\(_2\)O\(_4\) and LiFePO\(_4\) are attractive for the positive electrodes \[27\]. LiMn\(_2\)O\(_4\) has a cubic spinel structure, different from LiCoO\(_2\) and LiNiO\(_2\). Table 2-1 lists the comparison of these cathode materials. The spinel LiMn\(_2\)O\(_4\), although possessing 10% less capacity than LiCoO\(_2\), has an advantage in terms of cost and is perceived as being 'green' (that is, non-toxic and from abundant material source). In the LiMn\(_2\)O\(_4\) spinel structure (space-group: Fd3m), a cubic close-packed array of oxygen ions occupy the 32e position, Mn ions are located in the 16d site, and Li in the 8a site. The Mn ions have an octahedral coordination to the oxygen, and the MnO\(_6\) octahedral share edges in a three-dimensional host for the Li guest ions (Fig 2-10). The 8a tetrahedral site is situated furthest away from the 16d site of all the interstitial tetrahedral (8a, 8b and 48f) and octahedral (16c). Each of the 8a-tetrahedron faces is shared with an adjacent, vacant 16c site. This combination of structural features in the stoichiometric spinel compound constitutes a very stable structure. The empty tetrahedral and octahedral are interconnected with one another by common faces and edges to form
3D diffusion pathways for Li\(^+\) ion diffusion. Although LiMn\(_2\)O\(_4\) offers many advantages over LiCoO\(_2\), its implementation has been delayed because its capacity fades slowly. This fading is mainly caused by the lattice distortion resulting from the Jahn-Teller effect of the Mn\(^{3+}\) ion. This effect transforms the cubic crystal symmetry of the spinel electrode into tetragonal symmetry.\(^{[28]}\)

<table>
<thead>
<tr>
<th>Materials Properties</th>
<th>LiCoO(_2)</th>
<th>LiNiO(_2)</th>
<th>LiMn(_2)O(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td>Hexagonal</td>
<td>Hexagonal</td>
<td>Cubic (Spinel)</td>
</tr>
<tr>
<td></td>
<td>(a = 2.82) Å, (c = 14.05) Å</td>
<td>(a = 2.88) Å, (c = 14.18) Å</td>
<td>(a = 8.24) Å</td>
</tr>
<tr>
<td><strong>Theoretical capacity (mAh/g)</strong></td>
<td>274</td>
<td>275</td>
<td>148</td>
</tr>
<tr>
<td><strong>Practical capacity (mAh/g)</strong></td>
<td>120–130</td>
<td>120–150</td>
<td>100–120</td>
</tr>
<tr>
<td><strong>O(_2) evolution during overcharging</strong></td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td><strong>Diffusion coefficient (cm/s)</strong></td>
<td>(10^{-7}–10^{-9})</td>
<td>(10^{-7}–10^{-9})</td>
<td>(10^{-9}–10^{-11})</td>
</tr>
<tr>
<td><strong>Conductivity (S/cm)</strong></td>
<td>(10^{-2})</td>
<td>(10^{-1})</td>
<td>(10^{-6})</td>
</tr>
<tr>
<td><strong>Cost of the metal (US$/kg)</strong></td>
<td>50</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td><strong>Main advantages</strong></td>
<td>Straight forward synthesis</td>
<td>Highest capacity</td>
<td>3V plateau can be used as lithium source for anode</td>
</tr>
<tr>
<td></td>
<td>High cycle numbers</td>
<td>Good capacity retention</td>
<td></td>
</tr>
<tr>
<td><strong>Main drawbacks</strong></td>
<td>Reversibility highly dependent on synthesis conditions</td>
<td>Capacity fading upon long-term cycling</td>
<td>Synthesis is tricky</td>
</tr>
<tr>
<td></td>
<td>Capacity retention at high temperature (&gt;50°C)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A part of Li-Mn-O phase diagram \[^{30}\] is described in Figure 2-11. It is seen to involve many structures. This is related to the nature of Mn, which can have oxidation state II-VII. The most important oxidation states are II, IV and VII, in which II is the most stable valence. From a battery viewpoint, the spinel structures of interest in the Li-Mn-O phase diagram are located within the triangle of the MnO\(_2\)-LiMn\(_2\)O\(_4\)-Li\(_4\)Mn\(_5\)O\(_{12}\) tie-lines (Fig. 2-11b).

![Figure 2-10](image)

**Figure 2-10** Part of the unit cell of LiMn\(_2\)O\(_4\) showing the local structure around octahedrally coordinated manganese in an ideal spinel lattice. Mn-O bonds are represented by heavy solid lines; linear chains of Mn ions in neighboring edge-sharing octahedral are indicated by dashed lines\[^{29}\].

The electrochemical performance can be significantly improved by decreasing the amount of Mn\(^{3+}\) in the spinel compound. Another way is to introduce with heteroatoms, such as Al, Cr, Ni, Cu, Zn, Fe etc., to improve long-term cycleability and suppress capacity fades. It is well known that these materials show a greatly increased number of
charge-discharge cycles before failure when chromium (Cr), aluminum (Al), or other metal ions substitute for some of the manganese in the spinel crystal. The mechanism of failure and the role of metal substitution are still subjects of debate.

Figure 2-11 a) The Li–Mn–O phase diagram, b) a close-up of the Li₂MnO₃ – LiMnO₂ – λ-MnO₂ part of the Li-Mn-O phase diagram[30].

In the search for improved materials for positive electrodes, it has been recognized recently that NaSICON (a family of Na super-ionic conductors) or olivine (magnesium iron silicate) oxyanion scaffolded structures (Fig. 2-12)[27], built from corner-sharing MO₆ octahedral (where M is Fe, Ti, V or Nb) and XO₄\(^{n-}\) tetrahedral anions (where X is S, P, As, Mo or W), offer interesting possibilities. Polyoxyanionic structures possess M–O–X bonds; altering the nature of X will change (through an inductive effect) the iono-covalent character of the M–O bonding. In this way it is possible to systematically map and tune transition-metal redox potentials. In this way it is possible to systematically map and tune transition-metal redox potentials. For instance, with the use of the phosphate polyanions PO₄\(^{3-}\), the Fe\(^{3+}/Fe^{2+}\) and V\(^{4+}/V^{3+}\) redox couples lie at higher potentials than in the oxide form. One of the main drawbacks with using these materials
is their poor electronic conductivity, and this limitation had to be overcome through various materials processing approaches, including the use of carbon coatings, mechanical grinding or mixing, and low-temperature synthesis routes to obtain tailored particles. LiFePO₄, for example, can presently be used at 90% of its theoretical capacity (165 mA h g⁻¹) with decent rate capabilities, and thus is a serious candidate for the next generation of Li-ion cells [27].

Figure 2-12 On the left, expanded view of the framework built on FeO₆ octahedral and PO₄ tetrahedral, with Li ions in red. The FeO₆ octahedral are linked together through corner sharing in the (b, c) plane. On the right, restricted view of Li, Fe and P distribution between two distorted, h.c.p. (hexagonal close packed) oxygen-dense layers (PTd[LiFe]oct.O₄). LiO₆ octahedral share edges and Li ions may diffuse along [010] and [001]. [27]

The performance of lithium-ion battery electrodes can also be limited by mass transport of anions and cations through the pores of the electrodes. [31-32] Mass transport limitations generally worsen the utilization and rate capability of electroactive
Lithium transport is hindered by the slow transport kinetics of lithium from the bulk to the surface of the electroactive material particles. Fast transport kinetics would avoid ion depletion regions or concentration gradients that can degrade cell performance. Especially at high charge/discharge rates, large Li\(^+\) insertion or extraction fluxes at the surface, and slow Li\(^+\) transport in the bulk result in concentration polarization of Li\(^+\) within the electrode material. Besides the intrinsic properties of electrode materials, the architecture of the electrodes also influences the mass transport. When the ions are required to travel tortuous paths, it would impede mass transport and leads to polarization.

Therefore, one of the major challenges facing the development of novel lithium ion rechargeable batteries is the development of high performance electrode materials with excellent cycleability and minimal capacity fade. Nanostructured electrode materials with dual porous 3D structure have great potential to improve electrochemical behavior. Optimization of the electrode material parameters that influence ion kinetics at higher charge/discharge rate depends not only on the materials and synthesis methods but also on the microstructure of the electrode. The processing parameters such as the choice of the starting materials, doping elements and the heat treatment conditions are especially important to achieve a high crystallinity, to avoid phase impurities, and to adjust the correct oxygen stoichiometry. On the other hand, the architecture of 3D porous electrodes possess several features of interest in the design of novel battery materials, such as high accessible surface area, continuous networks, and features on the nanometer scale. The Li\(^+\) diffusion distances are correspondingly shorter, and the transport tortuosity is minimized; hence, less time is needed to achieve full charge or discharge at the same
current density. In addition, the larger surface areas of these electrode materials lower the current density, resulting in a decrease of concentration polarization. Furthermore, assembly of the ultra-fine electrode materials into continuous structures can enhance contacts and suppress free particle movement, so as to prevent small grains from penetrating the porous membrane separating the electrodes, which would result in short-circuiting the system and severe safety problems.

2.3 Reference


CHAPTER 3
EXPERIMENTAL TECHNIQUES

3.1 Chemical Synthesis Approaches

3.1.1 Sol-gel [1]

Sol-gel is a colloidal suspension that can be gelled to form a solid. The sol-gel process is a process for making glass/ceramic materials. The sol-gel process involves the transition of a system from a liquid (the colloidal “sol”) into a solid (the "gel") phase. The sol-gel process allows the fabrication of materials with a large variety of properties: ultra-fine or spherical shaped powders, monolithic ceramics and glasses, ceramic fibers, inorganic membranes, thin film coatings and extremely porous aerogels. Sol-gel chemistry is a remarkably versatile approach for fabricating materials. An overview of the sol-gel process is presented in a simplified chart (Figure 3-1).

The sol is a stable suspension of colloidal solid particles of a diameter of few hundred nm, usually inorganic metal salts, within a liquid phase. For a sol to exist, the solid particles, denser than the surrounding liquid, must be small enough for the forces responsible of dispersion to be greater than those of gravity. Practically, particles in a colloidal sol must have a size comprised between 2 nm and 200 nm; this corresponds to $10^3$ to $10^9$ atoms per particle. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, then the particles condense in a new phase, the gel, in which a solid macromolecule is immersed in a solvent.
Hydrolysis is a chemical reaction or process, in which a molecule is split into two parts by reacting with a molecule of water. In inorganic chemistry, the word is often applied to solutions of salts and the reactions by which they are converted to new ionic species or to precipitates (oxides, hydroxides, or salts). Many metal ions are strong Lewis acids, and in water they may undergo hydrolysis to form *basic salts*. Such salts contain a hydroxyl group (-OH) that is directly bound to the metal ion in place of a water ligand. This general reaction scheme can be seen in Figure 3-2 [\textsuperscript{3}].

Figure 3-1 Simplified Chart of sol-gel processes [2]
Figure 3-2 Schematic of the general hydrolysis reaction scheme.

The characteristics and properties of a particular sol-gel inorganic network are related to a number of factors that affect the rate of hydrolysis and condensation reactions, such as, pH, temperature and time of reaction, reagent concentrations, catalyst nature and concentration, H$_2$O/Si molar ratio (R), aging temperature and time, and drying \[^{[4-5]}\]. Of the factors listed above, pH, nature and concentration of catalyst, H$_2$O/Si molar ratio (R), and temperature have been identified as most important.

3.1.2. Hydrothermal Process

Among the low temperature methods, the hydrothermal method is very versatile for the synthesis of nano materials and has been well established. Although synthesis reactions can be carried out in a temperature range of 100° to 1000°C or more and in a pressure range of 1 atmosphere to several thousand atmospheres, most of the hydrothermal experiments are conducted below the supercritical temperature of water,
i.e. 374°C. The reactions can be carried out in water or in any other solvent. When water is used as a solvent, the process is called ‘hydrothermal process’ and when any solvent including water or organic solvents such as methanol, ethanol polyol, etc. are used, the process is termed ‘solvothermal process’. Thus the latter term encompasses all solvents including water. Nanophase oxides can be synthesized by the hydrothermal process and the main advantages of the hydrothermal method are⁶⁻⁷: (a) kinetics of reaction are greatly increased with a small increase in temperature, (b) new metastable products can be formed, (c) generally single crystals are obtained, (d) high purity products can be obtained from impure feedstocks, (e) no precipitants are needed in many cases and thus the process is cost-effective, (f) pollution is minimized because of the closed system conditions and reagents can be recycled, (g) hydroxylated clays and zeolite molecular sieves⁸ cannot be synthesized by any other method.

Hydrothermal experiments were carried out using cold-seal vessels where both the temperature and pressure can be controlled and Parr vessels (Parr Instrument Co., Moline, IL) where temperatures can be controlled precisely but not pressure. In the latter vessels autogeneous pressure was attained and this pressure depended on the temperature of treatment. Reactions were carried out in gold capsules or Teflon liners in the cold-seal and Parr vessels.

3.1.3. Templating Methods by Breath Figure Patterns

Template-directed synthesis is a convenient and versatile method for generating porous materials. It is also a cost-effective and high-throughput procedure that allows the complex topology present on the surface of a template to be duplicated in a single step. In
this technique, the template simply serves as a scaffold around which other kinds of materials are synthesized. By templating against supermolecular assemblies self-organized from small molecules, surfactant and block co-polymers, it has been possible to prepare various types of porous materials with pore sized in the range of 0.3-10 nm. With the use of mesoscale objects as templates, the dimension of these pores can be significantly extended to cover a wide range that spans from ~10 nm to 10 μm.

Apart from surfactant templating and colloidal crystal templating, recently, another templating method derived from breath figures patterns is emerging. Breath figures are the vapor condensation pattern that forms on the cold surface. This 2-dimensional hexagonal arrangement of micro-sized water droplets on cold surface was first investigated by Aitken[9] and Rayleigh[10-11] in the early 20 centuries. These breath figures are however not stable and eventually start coalescing. Until mid-1990s, Francois et al.[12] first successfully stabilized these hexagonal arrays in three dimensions by employing polystyrene-based polymer architectures such as star polymers and rod-coil block copolymers. Since then, scientists realized its potential application in different areas, such as optical bandgap materials, sensor, inverse opals and substrate for cell growth etc[13].

Detailed investigations suggests that this ordered hexagonal array was obtained by the encapsulation of water droplets on the liquid surface by a precipitating polymer layer, which prevented he water droplets from coalescence.
An attractive mechanism $^{[14]}$ for the formation of breath figure arrays was developed by Srinivasarao as shown in Figure 3-4: the formation and subsequent crystallization of breath figures was recognized as the caused for the hexagonally arranged arrays for air bubbles in micrometer-thick polymer films. When moist air is blown over a surface of the polymer solution, evaporative cooling decreases its temperature below dew points, and initiates the vapor condensation. Water droplets nucleate on the surface and subsequently grow. The water droplets sink into the solution if the solvents are less dense than water. A second layer of droplets subsequently form due to the cooling surface. When the surface temperature recovers to ambient temperature, the water droplets evaporate, and 3-D macroporous structure remains.
Figure 3-4 A model for the formation of the structure in polymer films. The images are color-coded, with blue and orange denoting low and high temperatures, respectively, relative to room temperature. (a) The conditions under which the experiment is performed. (b) Evaporation of the solvent cools the solution surface, thus initiating the nucleation and growth of moisture. (c) Because of the convective currents arising from the evaporation as well as from the airflow across the surface, the water droplets pack into a hexagonal array. (d to f) It is hypothesized that the ordered array sinks into the solution, thus leaving the surface of the solution free for the nucleation and growth of moisture to form another ordered array of water droplets. (g) When all of the solvent has evaporated, the film must return to room temperature, thus allowing the water droplets to evaporate as well while leaving behind the scaffold.
3.2 Characterization Techniques

3.2.1 Microstructure Characterization Techniques

3.2.1.1 Scanning Electron Microscope

SEM is a type of electron microscope capable of producing high resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample (size, shape and arrangement).

3.2.1.2 Transmission Electron Microscope

TEM is an imaging technique whereby a beam of electrons is focused onto a specimen so as to cause an enlarged version. It is widely used to characterize sample’s morphology including the size, shape and arrangement of the particles which make up the specimen as well as their relationship to each other on the scale of atomic diameters, and the obtain sample’s crystallographic information such as the arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects in areas a few nanometers in diameter.

3.1.1.3 X-ray Diffraction

X-rays are electromagnetic radiation of wavelength about 1 Å (10-10 m), which is about the same size as an atom. They occur in that portion of the electromagnetic spectrum between gamma-rays and the ultraviolet. The discovery of X-rays in 1895 enabled scientists to probe crystalline structure at the atomic level. X-ray diffraction has been in use in two main areas, for the fingerprint characterization of crystalline materials and the determination of their structure. Each crystalline solid has its unique
characteristic X-ray powder pattern which may be used for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure, i.e. how the atoms pack together in the crystalline state and what the interatomic distance and angle are etc. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science.

The basic of diffraction is Bragg’s law as shown in Figure 3-5, which describes the condition when diffraction occurs in a crystalline material:

\[ n\lambda = 2d \sin \theta \]  

where \( \lambda \) is the wavelength of the X-ray beam, \( d \) is the spacing between the planes in the atomic lattice, \( \theta \) is the angle between the incident ray and the scattering planes, and \( n \) is an integer. Waves that satisfy this condition interfere constructively and result in a reflected wave of significant intensity.

![Figure 3-5 Schematic of Diffraction of X-rays.](image)
3.1.1.4 BET Specific Surface Area

BET theory is a well-known rule for the physical adsorption of gas molecules on a solid surface. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET theory\textsuperscript{15} for the first time; “BET” consists of the first initials of their family names.

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed by Equation (3-2):

\[
\frac{1}{V_A[(P_0/P_s)-1]} = \frac{C - 1}{V_M C} \left(\frac{P_s}{P_0}\right) + \frac{1}{V_M C}
\]  

(3-2)

Where \( P_s \) and \( P_0 \) are the equilibrium and saturation pressure of adsorbates at the temperature of adsorption, \( V_A \) is the volume of gas adsorbed, \( V_M \) is the volume of the monolayer adsorbed, and \( C \) is the BET constant, which is expressed by Equation (2):

\[
C = \exp\left(\frac{E_1 - E_L}{RT}\right)
\]

(3-3)

\( E_1 \) is the heat of adsorption for the first layer, and \( E_L \) is that for the second and higher layers and is equal to the heat of liquefaction. \( E_1 - E_L \) is taken as the net heat of adsorption.

Equation (3-2) can be plotted as a straight line with \( 1/V_A [(P_0/P_s)-1] \) versus the relative pressure \( P_s/P_0 \) according to experimental results. This plot is called a BET plot. The linear relationship of this equation is maintained only in the range of 0.05<\( P_s/P_0 <0.35 \). The value of the slope, \( 1/V_M C \), and the intercept, \( (C-1)/V_M C \), of the
straight line are used to calculate the volume of monolayer adsorbed $V_M$ and the BET constant $C$.

The BET method or isotherm is widely used to determine the effective surface areas of solids materials with complicated shapes, such as porous powders, by physical adsorption of gas molecules. The observation of the so-called adsorption and desorption isotherms is used to determine the amount of gas molecules adsorbed to a surface. A total surface area $S_{\text{total}}$ and a specific area $S_{\text{BET}}$ are evaluated by the following equations:

$$S_{\text{total}} = \frac{V_M \cdot N_A \cdot A_{cs}}{M_V} \quad (3-4)$$

$$S_{\text{BET}} = \frac{S_{\text{total}}}{W} \quad (3-5)$$

Where $N_A$ is Avogadro’s number, $M_V$ is the molecular volume of adsorbed nitrogen, $W$ is the weight of adsorbent sample solid, and $A_{cs}$ is the cross section area occupied by adsorbed molecules. The cross-sectional area of the adsorbate nitrogen molecule is 0.162 nm$^2$.

3.2.2 Electrochemical Characterization Techniques

The chemical diffusion coefficient describes the relaxation of compositional gradients to achieve a homogeneous composition. This quantity is important in the case of many phenomena of practical interest, e.g., for corrosion processes or the performance of electrodes in batteries. Here two methods were described for determining the diffusion coefficient.

3.2.2.1 Galvanostatic Intermittent Titration Technique (GITT) [16-17]
In the galvanostatic mode, a constant current is applied which implies a time-independent concentration gradient of the mobile species in the sample just inside the interface with the electrolyte according to Fick’s first law.

\[ \Delta \delta = \frac{M}{zmF} \int_0^t Idt \]  

(3-6)

where M, m and F are the molecular weight of the sample, the original mass of the electrode and Faraday’s constant, respectively. the resolution is extremely high compared to typical measurements using balances. Changes of the order of less than \(10^{-10}\) g may be readily determined. The change in the cell voltage with time that results from this condition is measured. After an appropriate amount of current has been passed through the galvanic cell, the open circuit equilibrium cell voltage is determined and plotted as a function of the composition. Integration of this curve allows determination of the \(\Delta G\) value as a function of the composition. It is important to take the thermodynamic equilibrium cell voltage rather than the actual voltage while current is passing, which provides information about the energy loss due to various polarizations.

GITT also provides very comprehensive information about the kinetics parameter of the electrode by analysis of the electrical current. The current I, which is driven through the galvanic cell by an external current or voltage source, determines the number of electroactive species added to or taken away from the electrode and discharged at the electrode/electrolyte interface. A chemical diffusion process occurs within the electrode and the current correspond to the motion of mobile ionic species within the electrode just inside the phase boundary with the electrolyte (at \(x = 0\)).

\[ I = -Az_i qD \frac{\partial c_i}{\partial x} \]  

\(x = 0\),  

(3-7)
The GITT combines both transient and equilibrium measurements as illustrated in Figure 3-6. Starting with a homogeneous composition throughout the electrode, corresponding to the cell voltage $E_0$, a constant current $I_0$ is applied to the cell for a time interval $\tau$ in order to study the voltage as a function of time for the evaluation of $D$. This produces a constant concentration gradient of the mobile ions at the phase boundary with the electrolyte. The applied cell voltage increases or decrease (depending on the direction of the current) with the time in order to maintain the constant concentration gradient. A voltage drop due to other polarizations within the cell is superimposed, but the ohmic resistance $IR$ drop due to the current flux through the electrolyte and the interfaces remains constant with time and does not change the shape of the time dependence of the cell voltage. This behavior makes galvanostatic processes advantageous compared to other relaxation techniques which often involve large changes of the cell current, for example, in the case of a potential step which requires an initially large current which finally becomes zero. After such a titration pulse, the current flux is interrupted whereupon the composition has changed according to Equation (3-6). During the following equilibrium process, the voltage is directly related to the interfacial composition of the electrode and approaches a new steady state value $E_1$. It is found that the voltage transient follows a square root of time law. After the electrode has again reached equilibrium, the procedure may be repeated, making use of $E_1$ as a new starting voltage. The process continued until a phase change occurs in the electrode.
Figure 3-6 Principles of the galvanostatic intermittent titration technique (GITT) for evaluation of kinetic data of electrode. A constant current is applied and interrupted after certain time intervals $\tau$ until an equilibrium cell voltage is reached. During the current pulses, the transient voltage $E_t$ is observed as a function of time $t$ and analyzed to evaluate the chemical diffusion coefficient $D$. The steady-state equilibrium voltage is studied as a function of the composition.

In order to relate the time dependence of the voltage $E$ to the ionic transport in the electrode, Fick’s second law is solved for the concentration of the mobile ions at the interface $x=0$ which is observed experimentally by reading the cell voltage. With the appropriate initial and boundary conditions of a homogeneous concentration throughout the electrode at $t=0$, a constant concentration gradient at $x=0$ at any time and a zero
concentration gradient at the opposite surface of the cathode, and if \( t \ll L^2/D \), the following solution for the concentration of the mobile species at the interface is derived as a function of time:

\[
\frac{dc_i(x = 0, t)}{dt} = \frac{2I_0}{Az_iq(\tilde{D}\pi)^{1/2}} \quad (t \ll L^2 / \tilde{D}) 
\] (3-8)

Voltage provides information on the activity according to Nernst’s law, whereas the above Eqn indicates the time dependence of the concentration. By expanding above equation by \( dE \) and by introducing the relation between changes in the concentration and the stoichiometry,

\[ dc_i = (N_A/V_M)d\delta \] (3-9)

where \( N_A \) is Avogadro’s number and \( V_M \) is the molar volume of the electrode materials, the following equation could be obtained:

\[
\frac{dE}{dt} = \frac{2V_M^2I_0}{AFz_i(\tilde{D}\pi)^{1/2}} \frac{dE}{d\delta} \quad (t \ll L^2 / \tilde{D}) 
\] (3-10)

\( dE/d\delta \) is the slope of the coulometric titration curve at the given composition.

Hence, the expression for \( D \) as a function of the electrode composition is as follows:

\[
\tilde{D} = \frac{4}{\pi} \left( \frac{V_M^2I_0}{AFz_i} \right) \left[ \left( \frac{dE_s}{d\delta} \right)^2 \left( \frac{dE_t}{\sqrt{t}} \right)^2 \right] \quad t \ll L^2 / \tilde{D} 
\] (3-11)

3.2.2.2 Potential Step Chronoamperometry Techniques under Diffusion Control [18]

The calculation of the diffusion-limited current, and the concentration profile, involves the solution of the Fick’s first and second laws of linear diffusion equations:
\[
\frac{\partial C_i(x,t)}{\partial t} = \tilde{D}_i \frac{\partial^2 C_i(x,t)}{\partial^2 x}
\]  
(3-12)

Under the boundary conditions:

\[C_i(x,t) = C_i^* \quad (0 < x < L) \]  
(3-13)

\[\lim_{x \to L} C_i(x,t) = C_i^* \]  
(3-14)

\[C_i(0,t) = 0 \quad (\text{for } t > 0) \]  
(3-15)

The initial condition, (3-13) expressed the homogeneity of the solution before the experiment starts, and the semi-infinite condition, (3-14), is an assertion that regions distant from the electrode are unperturbed by the experiment. The third condition, (3-15), expresses the condition at the electrode surface after the potential transient.

And the flux at the electrode surface is proportional to the current,

\[-J_i(0,t) = \frac{i(t)}{nF \sigma} = \tilde{D}_i \left[ \frac{\partial C_i(x,t)}{\partial x} \right]_{x=0} \]  
(3-16)

By solving Fick’s first and second laws, the current-time response which is known as the Cottrell equation is derived.

\[i_d(t) = \frac{nFAD_i^{1/2}C_i^*}{\pi^{1/2}t^{1/2}} \quad (t << \frac{L^2}{D_i}) \]  
(3-17)

The effect of the depleting the electroactive species near the surface leads to an inverse \(t^{1/2}\) function. It is a mark of diffusive control over the rate of electrolysis.

Chronoamperometry has proven useful for the measurement of diffusion coefficients of electroactive species. An average value of \(it^{1/2}\) over a range of time is determined at an electrode the area of which is accurately known and with a solution of known
concentration. The diffusion coefficient can then be calculated from $i t^{1/2}$ via the Cotrrell equation.

3.2.2.3. Cyclic Voltammetry

Cyclic voltammetry is a kind of potentiodynamic electrochemical measurement. Being a specific type of voltammetry, it is used for studying the redox properties of chemicals and interfacial structures. For the majority of experiments the electroactive species is in the form of a solution.

The three-electrode method is the most widely used because the electrical potential of reference does not change easily during the measurement. This method uses a reference electrode, working electrode, and counter electrode (also called the secondary or auxiliary electrode). Electrolyte is usually added to the test solution to ensure sufficient conductivity. The combination of the solvent, electrolyte and specific working electrode material determines the range of the potential.

In cyclic voltammetry, the electrode potential follows a linearly ramping potential vs. time as shown Figure 3-7. The potential is measured between the reference electrode and the working electrode and the current is measured between the working electrode and the counter electrode. This data is then plotted as current ($i$) vs. potential ($E$). As shown in Figure 3-8, the forward scan produces a current peak for any analytes that can be reduced through the range of the potential scan. The current will increase as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface. As the applied potential is reversed, it will reach a potential that will reoxidize the product formed in the first reduction reaction,
and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak. As a result, information about the redox potential and electrochemical reaction rates of the compounds is obtained.

Figure 3-7 Cyclic potential sweep

Figure 3-8 Schematic cyclic voltammogram
3.2.2.4. Electrochemical Impedance Spectroscopy (EIS) \([16, 18]\)

Small-amplitude \((V<kT/q)\) ac impedance measurements are used to determine the bulk, and both the electrode and the grain boundary characteristics. The grain boundaries respond to a signal applied perpendicular to the boundary, as a capacitor and a resistor in parallel. For electrodes, the charge transfer process under small ac signals also exhibits a response that can be described by a capacitor connected with a resistor in parallel.

To assist in identifying the phenomena which determine the ac impedance spectrum one can vary parameters that affect the relaxation processes differently. The typical parameters are temperature, oxygen partial pressure, dc voltage applied on top of the ac one, length of MIEC and grain size. Raising the temperature will enhance the contribution of the process with the higher activation energy. Lowering the oxygen partial pressure, will promote oxygen diffusion limitation and the corresponding impedance. Applying a dc voltage does not affect the impedance of components which are ohmic, but changes the impedance of the nonohmic components. In particular, when the current depends exponentially on the voltage, as in the Butler-Volmer relations, the dc bias reduces the ac impedance. For a diffusion-limited process the dc bias increases the ac impedance. Increasing the grain size reduces the total grain boundary surface area per unit volume and should therefore reduce the impedance with the grain boundaries.

The shape of the ac impedance plots may deviate from that expected for the simple RC and Warburg elements. There are different reasons for deviations. Typical reasons are rough surfaces, constriction resistance, and distribution of elements with different characteristic parameters, mainly in the bulk. The constriction resistance is due to a smaller contact area of the electrode than the nominal electrode area. It has also been
shown that for a MIEC electrode the impedance of transfer of oxygen from the gas phase into the MIEC and the impedance of diffusion inside the MIEC, though coupled in series, do not yield separate parts in the Nyquist plot (imaginary part of impedance vs. real part of impedance).
3.3 Reference


CHAPTER 4
NANOSTRUCTURE ELECTRODES FOR LITHIUM ION BATTERIES

4.1 Synthesis and Characterization of Macroporous LiMn$_2$O$_4$ for Lithium Ion Batteries

4.1.1 Introduction

With increasing concerns about the impact on the environment of fossil fuel based combustion engines the development of electric and hybrid electric vehicles have become a declared priority of the US government. This entails an interest in the development of rechargeable batteries with adequate electrochemical properties that are affordable and environmentally benign. A great amount of research activity is aimed at finding new intercalation compounds that have high cycle life, high capacity and capacity retention.

The capacity of rechargeable Li-ion batteries is limited by the capacity and cycle life of the positive electrode. Spinel LiMn$_2$O$_4$ is a promising positive electrode material for rechargeable lithium-ion batteries because of its high reduction potential, low cost, and acceptable environmental impact as compared to LiCoO$_2$ [1,2]. To date, a variety of dry- (solid-state) and wet-chemical techniques have been explored to control the structural and hence electrochemical properties of LiMn$_2$O$_4$ [3-11]. Among these, glycine-nitrate process (GNP) seems to be one of the most attractive methods, which is a self-sustaining combustion process using metal nitrates as the oxidizer and glycine as the fuel [12]. Further, the glycine plays another important role: it complexes the metal cations to prevent selective precipitation in the precursor solution. Since all constituents of the
precursors can be homogeneously distributed at the molecular level in a solution, desired compositions can be readily obtained. To acquire the desired crystalline phases, a subsequent short-time annealing can be used. In contrast, the solid-state techniques and wet-chemical methods (such as sol-gel and Pechini processes) often involve a long processing time at high temperatures to form the required crystalline phases.

Homogeneity of the starting material is critical point to determine purity of final product. If not, undesired compounds may be formed as impurities. It is well known that recalcinations and subsequent repeated regrinding were significantly necessary to prepare high purity transition metal oxides. From these reasons, soft chemistry routes, such as emulsion drying and hydrothermal methods, were employed to synthesize high purity double transition metal oxide electrode materials, for lithium-ion batteries.

In particular, the vigorous gas evolution of a combustion reaction often produces highly-open, nano-structured powders; the detailed microstructures of the powders, however, depends critically on the combustion parameters such as the ratio of fuel to oxidant, cation concentration to fuel, and the amount and evolution rate of the gases released during a combustion process.

While a number of researchers have reported the syntheses of the intercalation compounds using the combustion process [7-11], the role of gas evolution in creating porous structures with high surface area is yet to be investigated. The nano-porous structures with the high porosity and large surface area are highly desirable for electrode applications in solid state electrochemical systems. In this communication, we report the structural and electrochemical properties of highly open nano-structured LiMn$_2$O$_4$ with spinel structure prepared by a modified glycine-nitrate process.
4.1.2 Experimental

4.1.2.1 Preparation of Macroporous LiMn$_2$O$_4$

Stoichiometric amounts of LiNO$_3$ and Mn(CH$_3$COO)$_2$-4H$_2$O were dissolved in distilled water. Nitric acid with the same mole of acetate anions was added to the solution. The molar ratio of glycine to nitrate was optimized during the range from 0.5 to 2. (shown in Table 4-1) The resulting solution was heated on a hot plate to evaporate the excess solvent, producing the viscous resin and then dark brownish foam. When further heated, it ignited, yielding a voluminous, black, sponge-like ash. The resulting ash was subsequently fired in air at 800°C for 2 hrs. In particular, the precursor Mn(CH$_3$COO)$_2$-4H$_2$O was chosen instead of Mn(NO$_3$)$_2$·xH$_2$O because it produces a greater amount of gas during combustion, which is favorable to producing highly open porous microstructures, and at the same time it obviates the ambiguity of the amount of crystalline water in the manganese salt.

Table 4-1 Experiment conditions for glycine-nitrate combustion process

<table>
<thead>
<tr>
<th>Condition or Sample No.</th>
<th>[Li$^+$]+[Mn$^{2+}$]</th>
<th>Ratio of fuel/oxidant (glycine/nitrate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.5 M</td>
<td>0.5</td>
</tr>
<tr>
<td>S2</td>
<td>0.5 M</td>
<td>1.0</td>
</tr>
<tr>
<td>S3</td>
<td>0.5 M</td>
<td>1.5</td>
</tr>
<tr>
<td>S4</td>
<td>0.5 M</td>
<td>2.0</td>
</tr>
</tbody>
</table>
For the sake of comparison, spinel LiMn$_2$O$_4$ was also fabricated using a conventional solid-state reaction. LiMn$_2$O$_4$ powder was prepared by heating a pressed mixture of stoichiometric amounts of LiNO$_3$ and Mn$_2$O$_3$ at 850 °C for 48 hrs in air with intermittent grindings, followed by a ball-milling for 24 hrs. The average particle size of the resulting powder was about 5µm as estimated from an SEM (Hitachi S-800 Scanning Electron Microscope) observations.

4.1.2.2 Characterization of Macroporous LiMn$_2$O$_4$

X-ray powder diffraction (XRD) patterns were recorded with Philips PW-1800 X-Ray Diffractometry (with CuKα radiation). The chemical compositions of the samples were analyzed using an inductively coupled plasma (ICP) technique (Perkinelmer Optima 3000DV) to estimate the ratio of Mn to Li. The morphology was revealed using an SEM and a TEM (Hitachi HF-2000 Transmission Electron Microscope). The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method (Micromeretics ASAP 2000).

The tapping density of the powders was roughly estimated by placing a known mass of the powder (500 mg) in a glass tube (0.5 cm diam.) and tapping it 300 times on a lab bench. The density of the powder exhibited a slow relaxation approach to the final packing state, i.e. after 300 tappings the density (or volume) of the powder showed little change with the number of tapping, which was taken as the tapping density of the powder.

Two-electrode electrochemical cells were employed for electrochemical measurements using lithium foils as the counter and reference electrode. The working electrode was composed of calcined LiMn$_2$O$_4$ (78 wt%), carbon black (10 wt%), and
polyvinylidene fluoride (PVDF) binder (12 wt%). The mixture was prepared by ball milling and the slurry was cast on Al foil, followed by drying at 180 °C in vacuum for 24 h and uniaxial pressing between 2 flat plates at ~500 psi for 5 min. The electrode loading was 2.04 mg of spinel LiMn$_2$O$_4$ in a square centimeter of Al. A Celgard 2400 separator, wetted with 1M solution of LiPF$_6$ in a 50/50 (v/o) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), was sandwiched between an LiMn$_2$O$_4$ working electrode and a lithium counter electrode. All cells were assembled and tested in a glove box (Vacuum Atmospheres Company) filled with purified argon gas. The O$_2$ and H$_2$O content were kept below 1 ppm. A Solartron 1285 potentiostat was employed to carry out the cyclic voltametry, chronoamperometry, and galvanostatic intermittent titration technique (GITT). And, a Maccor battery test system (Model 2300) was used to evaluate the rate capability and cyclability.

In particular, for the rate capability test, a charging current of 61.2 μA/cm$^2$ (C/4 rate; a nominal specific capacity of 120 mAh/g was assumed to convert the current density into C rate. C-rate is a charge or discharge current rate of a battery expressed in amperes. It is a numerically a fraction or a multiple of the rated capacity of the battery expressed in ampere-hours.) was applied until the cell voltage reached 4.4 V (vs. Li/Li$^+$). Subsequently, discharging currents in the range of 61.2 μA/cm$^2$ (C/4) to 4.90 mA/cm$^2$ (20C) were applied until the cell voltage reached 3.3 V (vs. Li/Li$^+$). A GITT was employed to estimate the chemical diffusion coefficient of lithium in the solid state$^{[13]}$. In a typical measurement, a constant current of 50 μA/cm$^2$ was applied to the cell for 1000 s, and then was interrupted for 2000 s to allow the cell to equilibrate. The voltage profile during current application/interruption was recorded and the voltage at the end of current
interruption was taken as the open circuit voltage. The current application/interruption was repeated until the (closed circuit) potential reached 3.0 (V vs. Li/Li⁺). The degree of discharge (DOD) or lithium content 1-δ in Li₁₋δMn₂O₄ was estimated from the mass of the oxide and the charge transferred during current application.

4.1.3 Microscopic Properties

The microstructures of the LiMn₂O₄ powders were optimized by varying the fuel/oxidant ratio. The ratio of the fuel(glycine) to oxidant(nitrate ions) were set 0.5, 1, 1.5 and 2. Shown in Figure 4-1 are the resulting SEM images of the calcined LiMn₂O₄ powders prepared with different fuel/oxidant ratio. The microstructures with lower fuel/oxidant ratio exhibit highly porous structure. On contrary, the microstructure with high fuel/oxidant ratio exhibit less porosity. It may be because that the excess fuel residues promote sintering when powders were subsequently calcinated at high temperature at 800°C. The calcined powders prepared with the f/o ration of 1 exhibited interconnected and highly open porous microstructures (Figure 4-1c,d).
S1: Fuel/oxidant=0.5

S2: Fuel/ratio=1

Figure 4-1 SEM images of calcined LiMn$_2$O$_4$ powders at 800°C: (a-b) low and high magnification of SEM images of LiMn$_2$O$_4$ powders prepared under sample S1 condition; (c-d) low and high magnification of SEM images of LiMn$_2$O$_4$ powders prepared under sample S2 condition.
Figure 4-1(continued) SEM images of calcined LiMn$_2$O$_4$ powders at 800°C: (e-f) low and high magnification of SEM images of LiMn$_2$O$_4$ powders prepared under sample S3 condition; (g-h) low and high magnification of SEM images of LiMn$_2$O$_4$ powders prepared under sample S4 condition.

S3: Fuel/oxidant=1.5

S4: Fuel/oxidant=2
Lithium is easily evaporated during combustion process. The more intense the combustion reaction is, the more weight loss of lithium would be expected. Hence excess lithium ions were considered in the preparation. Shown in Figure 4-2 to 4-4 are the X-ray diffraction patterns of as-synthesized and calcined powders for sample S2-S4. It is clear that there exist Mn$_3$O$_4$ and Mn$_2$O$_3$ phases with lower valence state of Mn than LiMn$_2$O$_4$ in all the as-synthesized powder along with some unidentified phases, probably the distorted LiMn$_2$O$_4$. After calcination in air at 800°C for 2 hrs, the desired crystalline spinel structure of LiMn$_2$O$_4$ was formed as shown in both Figure 4-3d and Figure 4-4b. But there were still unknown peaks in the calcined sample S2 as shown in Figure 4-2b. The most highly crystalline spinel phase was obtained from the sample S2.

Highly crystalline LiMn$_2$O$_4$ spinel structure could be obtained by annealing at temperature of 800°C. On the other hand, the nanoparticles would grow at high temperature due to the high surface energy. It would sustain particle growing to decrease the annealing temperature. Figure 4-3a-d shows the XRD spectra as the annealing temperature for the sample S2. At the temperature of 500°C, the spinel structure has formed. As temperature increases, the peaks become sharper and more intense. It was also observed that the peak positions moved to lower angle.

Based upon the SEM and XRD results, the S2 samples exhibited optimal microstructure and crystal structure. And more studies were carried out for the S2 samples.

From the Rietveld refinement method, the lattice parameter of our spinel LiMn$_2$O$_4$ from Figure 4-3d was calculated to be 8.237 Å. Moreover, The ICP analysis showed that the atomic ratio of Mn to Li is 2.04. Both lattice parameter and atomic ratio of Mn to Li
for our LiMn$_2$O$_4$ are similar to those reported in the literature for the conventional stoichiometric LiMn$_2$O$_4$ [8,11]. The tapping density of our powder was about 0.72 g/cm$^3$, which is much smaller than a typical value of 2.5~3.0 g/cm$^3$ for the commercially available positive electrodes, probably due to the highly-porous feature of our powder. The adjustment of the (micro-)structure of the GNP-prepared powder, including the size distribution of the pore as well as the fragmented particles after mechanical grinding, is expected to increase the tapping density of the powder.

Figure 4-2 X-Ray diffractograms of as-synthesized and calcined LiMn$_2$O$_4$ powders at 800°C for 2hrs for sample S1.
Figure 4-3 X-Ray diffractograms of as-synthesized and calcined LiMn$_2$O$_4$ powders at 500°C, 700°C and 800°C for 2hrs for sample S2.
Figure 4-4 X-Ray diffractograms of as-synthesized and calcined LiMn$_2$O$_4$ powders at 800°C for 2hrs for sample S3.

Shown in Figure 4-5 are some typical TEM images of the as-synthesized and calcined LiMn$_2$O$_4$ powders for sample 2. The primary particle size of the as-synthesized powders (Figure 4-5(a)) is around 10 nm with visible agglomerations. The average particle size increased to about 100 nm after firing at 800°C for 2hrs, as shown in Figure 4-5(b). Figure 4-1c-d depicts the typical morphologies of calcined powders which are characteristic of a macro-porous structure with uniformly distributed interconnected
pores of about 500 nm in diameter. The as-synthesized and calcined powders typically have surface areas of 17.0 and 5.9 m² g⁻¹, respectively, as measured by the BET technique. Based on the BET results, the equivalent particle sizes of the as-synthesized and calcined powders were estimated to be 82 nm and 236 nm, respectively. The difference of the particle size between the observed ones and calculated ones is aroused by the assumption for the calculation that the particles are spherical and there is no contact among the particles. The calculated particle sizes match satisfactorily the observed particle sizes from TEM, in spite of the possible overestimation of the calculated particle sizes due to the roughness of the particle (Figure 4-5) and interconnection between the particles (Figure 4-1c). This high porosity of the LiMn₂O₄ is attributed to the vigorous gas evolution (H₂O, N₂ and CO₂) during the combustion synthesis.

\[
2\text{Mn(}CH_3\text{COO)}_2 + 4\text{HNO}_3 + \text{LiNO}_3 + 2\text{NH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{combustion in air}} \text{LiMn}_2\text{O}_4 + 13\text{H}_2\text{O}↑ + (7/2)\text{N}_2↑ + 12\text{CO}_2↑ \tag{4-1}
\]

This microstructural and morphological disturbance/distortion are expected to facilitate mass and charge transport through the porous electrodes during lithium battery operation [14-16].
Figure 4-5. TEM images of (a) as-synthesized and (b) calcined powders
4.1.4 Electrochemical Behavior of Macroporous LiMn$_2$O$_4$

Lithium insertion (discharge) / extraction (charge) reaction into / from spinel LiMn$_2$O$_4$ proceeds reversibly according to the following equation \cite{17}.

\[
\begin{align*}
\text{Li}_x\text{Mn}_2\text{O}_4 + \Delta x \text{Li}^+ + \Delta x e^- & \xrightarrow{\text{discharge (lithium insertion)}} \text{Li}_{x+\Delta x}\text{Mn}_2\text{O}_4 \\
& \xleftarrow{\text{charge (lithium extraction)}}
\end{align*}
\]

4.1.4.1 Reversibility

In order to evaluate the properties of the GNP-prepared LiMn$_2$O$_4$ powder during the electrochemical lithium insertion / extraction, a variety of electrochemical testing were performed on S2 samples calcined at 800°C. Shown in Figure 4-6 is a typical cyclic voltammogram of the calcined powder at a scan rate of 0.1 mV/s. Two anodic peaks at 4.08 and 4.22 V (vs. Li/Li$^+$) and the corresponding two cathodic peaks at 3.93 and 4.05 V (vs. Li/Li$^+$) are ascribed to the lithium extraction and insertion processes, respectively.

![Typical cyclic voltammogram of calcined spinel LiMn$_2$O$_4$ powders](image)

Figure 4-6 Typical cyclic voltammogram of calcined spinel LiMn$_2$O$_4$ powders
Shown in Figure 4-7 is a typical galvanostatic charge/discharge profile of the calcined powders at a current density of 49.0 $\mu$Acm$^{-2}$ (C/5 rate), showing a two-staged lithium insertion/deinsertion behavior, consistent with the cyclic voltametry result. The two quasi-potential plateaus are a characteristic of a well-defined LiMn$_2$O$_4$ spinel $^{[1,2]}$. The specific reversible capacity is about 112 mAh$^{-1}$ (228 $\mu$Ahcm$^{-2}$) during both charging and discharging processes, implying reversible lithiation/delithiation of the calcined LiMn$_2$O$_4$ powders.

![Figure 4-7 Galvanostatic charge/discharge curve at the current density of 49.0 $\mu$A/cm$^2$ (C/5 Rate).](image)
The theoretical specific capacity of LiMn$_2$O$_4$ is 148 mAh/g when lithium is fully extracted to form $\lambda$-MnO$_2$. The discrepancy between the theoretical and experimental specific capacities is due probably to kinetic limitation of the lithium extraction reaction at relative fast lithium extraction process as well as the difficulty in full electrochemical extraction of lithium to form $\lambda$-MnO$_2$ at practical potential ($< 5$ V vs. Li/Li$^+$) $^{[17]}$. When we consider the mass of binder (12 wt%) and current collector (10 wt%), the theoretical and experimental capacities per unit mass of the composite electrode become 115.4 mAh$^{-1}$ and 87.4 mAh$^{-1}$, respectively. On the other hand, the theoretical capacity density (volumetric) of the ideally dense LiMn$_2$O$_4$ is known to be 634 mAh/cc $^{[17]}$ while the experimental capacity density of our GNP-prepared LiMn$_2$O$_4$ porous composite (including additives such as binder and carbon) was estimated to be 120 mAh/cc. The much smaller capacity density of our powder than pure dense LiMn$_2$O$_4$ is attributed to the large amount of additives as well as the porous feature of our powder and a pressed composite electrode.

4.1.4.2 Rate Capability

The rate capability of the same powders during discharging processes is shown in Figure 4-8. At discharging rates of C/4 (61.2 $\mu$A/cm$^2$), C/2 (122.4), 1C (244.8), 2C (489.6), 3C (734.4), 5C (1224), and 10C (2448) the cell delivered specific capacities of 108 (220), 104 (212), 102 (208), 89 (182), 83 (169), 76 (155), and 57 mAh$^{-1}$ (116 $\mu$Ahcm$^{-2}$), respectively. In particular, more than 50% of the reversible capacity at C/4 rate can be discharged at 10C rate. This rate capability is higher than the rate capability for the spinel LiMn$_2$O$_4$ prepared by a conventional solid-state reaction, as shown in Figure 4-8b, as well as those reported for the spinels fabricated by the similar solid-state
reactions \cite{18,19}, but smaller than those for the spinels created by sophisticated techniques such as a template method \cite{20} and spray-drying process \cite{21}. Nevertheless, the combustion process has a great potential to create a variety of morphologies with different rate capacities because the rate capability depends critically on the electrochemically-active surface area and/or pore size of the powders. In this combustion process, the surface area and porosity of the powders are critically affected by the ratio of the precursor to fuel, which determines the rate of gas evolution during the combustion process.

Figure 4-8 (a) Dependence of voltage profile on applied current density and (b) variation of fractional discharging capacity retention in discharging rate (open circle), reconstructed from Fig. 4-8a. For the sake of comparison, the discharging capacity retention of the LiMn$_2$O$_4$ prepared by a conventional solid-state reaction was included (open square). The specific discharge capacities at C/4 rate of two samples prepared by GNP and solid-state reaction were 108 and 112 mAh/g, respectively.
4.1.4.3 Cycling Studies

Shown in Figure 4-9 is the cycling behavior of the calcined powder at a current density of 122.4 μA/cm² (C/2 rate). The discharging capacity retention was about 90% at the 20th cycle and half of the capacity loss occurred during the first several cycles. This relatively large capacity fade is typical for the spinel LiMn₂O₄, making it impractical for real applications. Nevertheless, recent work has shown that the cyclability can be significantly improved by introducing dopants to the LiMn₂O₄ [22,23]. The effects of dopants on long-term cycling performance of GNP-prepared powders are still under investigation.

Figure 4-9 Dependence of discharging capacity retention of calcined powders on the number of cycles at the cycling rate of 122.4 μA/cm² (C/2).
4.1.4.4 Electrode Kinetics

In order to explore the kinetics of lithium transport through the electrode materials, chronoamperometry was performed between 3.9 and 4.2 V (vs. Li/Li⁺). Shown in Figure 4-10 are the $I \cdot t^{1/2}$ vs. log $t$ plots according to Cottrell Equation (3-17). However, there is no plateau region (i.e. no Cottrell region) throughout the intercalation/deintercalation time, indicating that the overall process was not controlled by lithium diffusion (e.g., the interfacial resistance could be significant as compared to diffusional resistance [24]). This further implies that the lithium transport through the calcined LiMn$_2$O$_4$ electrode is possibly controlled by slow interfacial reaction during the chronoamperometric measurement [24,25]. Under the circumstances, it is unlikely that the analysis of the chronoamperometric curves gives us reliable values of diffusion coefficient. Instead, we adopted a GITT to evaluate the diffusion coefficient.

Figure 4-10 Typical chronoamperometric curves of calcined powders.
Shown in Figure 4-11(a) is a typical voltage transient during a current application and a subsequent current interruption in the GITT experiment. In a very short time range, where semi-infinite lithium diffusion in the solid state occurs, the cell voltage is proportional to the square root of time, as suggested by a linear regression analysis (insert in Figure 4-11(a)). From the potential transient (e.g. insert in Figure 4-11(a)) and the coulometric titration curve (Figure 4-11(b)), the chemical diffusion coefficient of lithium was determined as a function of lithium content (1-δ) \(^{[13]}\). The value of diffusion coefficient ranged from \(10^{-10}\) to \(10^{-13}\) cm\(^2\)/s. In particular, the dependence of the diffusion coefficient on (1-δ) shows two minima in the (1-δ) regions where quasi-potential plateaus are observed, which are attributed to high attractive interactions related to lithium intercalation process \(^{[25]}\).

**4.1.5 Conclusion**

Nanostructured LiMn\(_2\)O\(_4\) spinel has been successfully synthesized using a glycine-nitrate combustion process followed by a short-time calcination. The calcined powder retained a porous nanostructure but with improved crystallinity and showed quite reversible lithiation and delithiation during cycling. The obtainable reversible capacity of the calcined powder was about 112 mAh\(^{-1}\). In particular, more than 50% of the reversible capacity (57 mAh\(^{-1}\)) could be delivered at a high discharge rate of 2.44 mA/cm\(^2\) (10C), which is a higher rate capability than those reported for the spinel LiMn\(_2\)O\(_4\) prepared by conventional solid-state reactions. The glycine-nitrate process appears to be an attractive method for fabrication of cost-effective nanostructured electrodes for lithium secondary batteries.
Figure 4-11. (a) Typical voltage transient during a current application and a subsequent current interruption in the GITT experiment and cell voltage (V) vs. time$^{1/2}$ ($t^{1/2}$) plot in a very short time range (insert in Fig. 8(a)) showing the linear relationship between V and $t^{1/2}$, and (b) open circuit voltage obtained from the GITT experiment (open circle) and chemical diffusion coefficient (solid circle) as a function of lithium content.
4.2 Nanostructured Tin dioxide Negative Electrode for Lithium Ion Batteries

Nanostructured tin oxide thin films with columnar grains were deposited on gold-coated silicon substrates using combustion CVD method. Microscopy revealed that the columnar grains were covered by nanoparticles less than 20 nm. The electrochemical behavior of the as-prepared thin film electrodes was examined against a lithium counter electrode. These thin film electrodes exhibited substantially higher specific capacity than those prepared by other techniques. The capacity retention was excellent; the capacity increased from an initial value of about 360 μA/cm²-μm gradually to a maximum value of ~490 μA/cm²-μm during cycling. The reversible capacity was about 460 μA/cm²-μm after 80 cycles at a charge/discharge rate of 0.3 mA/cm². When discharged at 0.9 mA/cm², the capacity retention obtained was about 64% of the capacity at 0.3 mA/cm². The good electrochemical performance is attributed to the unique nanostructure with longitudinal and radial connectivity of active materials.

4.2.1 Introduction

Tin oxide has been regarded as a potential substitute for commercial carbon based materials due to its high storage capacity (781 mAh/g for tin dioxide vs. 372 mAh/g for graphite). However, the large volume change (up to 300%) associated with alloying and de-alloying causes critical mechanical damage to the electrode, resulting in loss of capacity and rechargeability.[27-29] Potential solutions to the pulverization problem includes modifying the material chemistry through doping, and designing novel and stable architectures using new fabrication techniques. In this work, we report a tin oxide thin film electrode with nanostructured, columnar grains fabricated using combustion
CVD process. The as-prepared SnO$_2$ electrode demonstrated high reversible capacity and excellent cycleability.

Prior investigations $^{[30-31]}$ suggested that the pulverization problems associated with the large volume difference between the lithiated and lithium-free host can be lessened by using a smaller particle (or small grain within these particles) morphology to reduce the absolute local volume changes of each reactive grain and by introducing a matrix (such as TCO $^{[32]}$) to confine volume change and reduce local mechanical stresses. Though the small particle size tin outperforms the coarse one, mobile Sn regions have the tendency to aggregate in subsequent cycling process.$^{[29, 33]}$ As a result, the formation of large tin domains makes the material sensitive to cracking and crumbling and thus degenerating the capacity. Brousse et al. $^{[34]}$ reported that Li alloys would suffer from large Li-driven volume swings due to the growth of large clusters; and that the continuous percolation paths, and even worse the intergrain electronic contact across the composite, might also degrade electrode performance and cause electrode failure.

Recent investigations showed that nanostructured electrodes (e.g., nanotubes and nanowires) exhibited improved electrochemical behavior (e.g., superior rate capabilities and cycleability).$^{[35-37]}$ The performance of lithium-ion battery electrodes could also be limited by mass transport of anions and cations through the bulk of the electrodes.$^{[38-39]}$ Mass transport limitations generally worsen the utilization and rate capability of electroactive materials.$^{[40]}$ While, interfacial kinetics was dramatically facilitated by the high surface area of these nanostructured materials. Electrodes with open, porous and connective architecture possess several features of interest in the design of novel battery materials, such as high accessible surface area, easy accessibility, connectivity of
electroactive materials, and features on the nanometer scale. The Li$^+$ diffusion distances are correspondingly shorter, and the transport tortuosity is minimized; hence, less time is needed to achieve full charge or discharge at the same current density. In addition, the larger surface areas of these electrode materials lower the local current density, resulting in a decrease of concentration polarization. Furthermore, assembly of the ultra-fine electrode materials into continuous structures can enhance contacts and suppress free particle movement, so as to hinder aggregation of mobile electrode materials. Thus, the major challenge is to fabricate electrochemically active while structurally stable SnO$_2$ architectures. Here we report SnO$_2$ thin films with nanostructured columnar grains as negative electrodes for lithium ion batteries. The tin oxide thin films were deposited on gold-coated silicon substrates by a combustion chemical vapor deposition (CVD) process. Combustion CVD is versatile in synthesis nanostructured materials, which has been employed to prepare either nanosized powders or a variety of nanostructured ceramic films with controllable thickness and porosity for solid oxide fuel cells and gas sensors. SnO$_2$ thin films for lithium ion batteries deposited using combustion CVD are mechanically strong, electrochemically stable and demonstrate high reversible capacities.

4.2.2 Experimental

4.2.2.1 Preparation of SnO$_2$ Thin Film

SnO$_2$ thin film electrodes were prepared by a combustion CVD process as described elsewhere. Silicon substrates (4 mm × 4 mm) were cut from commercial 4-inch wafer. The Si substrates were then coated with gold for 10 minutes by DC sputtering. The precursor solution was prepared by dissolving tin(II)-2-ethylhexanoate
(Aldrich) in absolute ethanol. The resulting solution was then pumped into a specially designed atomizer, where the precursor solution was mixed with high-pressure oxygen and atomized to produce a microscale mist. The solute rich fine mist was combusted with the help of small CH₄/O₂ pilot flames. During deposition, the Au/Si(100) substrates were placed in the appropriate temperature zone of the combustion flame. Depositions were performed at 700°C for 5 minutes. No additional annealing is needed for the as-deposited samples.

4.2.2.2 Characterization of SnO₂ Thin Film

The crystallographic structure of the SnO₂ thin film was studied by X-ray powder diffraction (XRD) with Philips PW-1800 X-ray Diffractometry at a scanning rate of 0.02° per minute. The morphology of the as-deposited films was observed by a scanning electron microscopy (SEM Hitachi S-800).

A two-electrode cell configuration (Hohsen test cell, Hohsen Corp. Japan) was used for electrochemical measurements. The as-prepared SnO₂ film served as working electrode. Copper foil, as a current collector, was mechanically attached to the backside of the silicon substrate (shown in Figure 4-12). Lithium foil was used as the counter electrode. The electrolyte was a 50:50(v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) containing a 1M solution of LiPF₆. All cells were assembled and tested in a glove box (VAC, USA) under purified argon atmosphere. The electrochemical behaviors were measured by a Maccor battery test system (Model 2300). The SnO₂ electrodes were galvanostatically charged (Li⁺ insertion) and discharged (Li⁺ extraction) in the voltage range of 0.1-1 V versus Li/Li⁺, at a current density ranging from 100 μA/cm² up to 900 μA/cm².
4.2.3 Microscopic Features and Phase Structure

Shown in Figure 4-13 is the X-ray diffraction pattern of the as-prepared tin oxide thin film on a Si substrate. The observed peaks correspond to a typical SnO$_2$ cassiterite phase (JCPDS 41-1445) except the two very sharp and intense peaks, which are attributed to the underneath Si(100) wafer. Au was not detected on the XRD spectra probably because the thickness of sputtered Au is under the detecting limit.
Figure 4-13. XRD pattern of as-prepared nanostructured tin oxide thin film.

Shown in Figure 4-14 are some typical SEM images of the nanostructured tin-oxide thin film. As revealed in the side view (Figure 4-14a), the tin oxide film consisted of columnar grains of about 0.5 μm to 2 μm wide. The columnar grains grew from the substrate independently and separated from each other, leaving large spaces in between. Thickness of the film was about 2-5 μm. Figure 4-14b shows top view of the tin oxide film. The inset is a higher magnification image, indicating the surface of each grain is covered by nanoparticles less than 20 nm.
Figure 4-14. SEM images of nanostructured tin oxide thin film a) side view, and b) top view. Insets are enlarged images.

4.2.4 Electrochemical Properties

4.2.4.1 Alloying Mechanism

The as-prepared nanostructured tin oxide thin film was assembled into a test cell (against lithium) to evaluate the electrochemical performance. Shown in Figure 4-15 are the cell voltages of the first charging/discharging cycle as a function of the capacity of
the nanostructured tin oxide thin film at a constant current density of 0.1 mA/cm². The galvanostatic charging and discharging experiments were conducted between potential limits of 0.1 and 1 V vs. Li⁺/Li. Prior to charge/discharge experiments, the electrode were charged from the open-circuit potential to the lower potential limit of 0.1 V, and then discharged back to the upper limit of 1 V. The charge/discharge characteristic curve of tin oxide thin film can be divided into 2 regions on the first charge curve: a typical irreversible plateau at 0.8-0.9 V in the first charge followed by a monotonous decrease to 0.1 V. The two-phase reaction in the tin oxide thin film can be described as follows,\textsuperscript{[3]}

\begin{align*}
4\text{Li}^+ + 4\text{e}^- + \text{SnO}_2 &\rightarrow 2\text{Li}_2\text{O} + \text{Sn} \quad \text{[4-3]} \\
x\text{Li}^+ + xe^- + \text{Sn} &\leftrightarrow \text{Li}_x\text{Sn} \quad 0 \leq x \leq 4.4 \quad \text{[4-4]}
\end{align*}

which involves a two-step process: a reduction of the tin oxide and lithium ion to metallic tin and lithium oxide, and an alloying of the tin with lithium. The formation of the lithium oxide and metallic tin is an irreversible reaction responsible for the irreversible capacity in these systems. The reversible alloying and de-alloying processes offer reversible storage capacity.
Figure 4-15. The first potential profiles vs. the capacity of nanostructured tin oxide thin film tested at a constant current density of 0.1 mA/cm².

In generally, a plateau was found at 1.0V vs. Li or above, and then a second plateau was found at about 0.8 V vs Li in the first charging curve for almost tin oxide electrodes. The first plateau corresponds to the decomposition of SnO₂ to Sn. The second plateau corresponds to the beginning of alloying between Lithium and tin. Sometimes, the first plateau was not so obvious for pure tin oxide thin film, because tin dioxide is a semiconductor, and its electronic conductivity is less than that of a composite disk electrode which consists of electro-conductive additives. In our work, only the second plateau in the charging curves was detected for almost all our samples. There is a slight slope change at about 1.5 V in Figure 4-15 which may correspond to the decomposition
of tin oxide. Similar charging curves of tin oxide electrodes could also be found in the Reference\textsuperscript{[32, 45-47]}. The difference was shown clearly in Reference\textsuperscript{[45]} by comparing the charging curves between a SnO\textsubscript{2} thin film and a Si-doped SnO\textsubscript{2} thin film. There was no obvious plateau above 1.0 V for the undoped SnO\textsubscript{2} thin film. But there was a plateau above 1.0V for the Si-doped SnO\textsubscript{2} thin film.

In the first charge-discharge process, the charge capacity was about 684 \(\mu\text{A h/cm}^{2}-\mu\text{m}\). And the discharge capacity was about 352.8 \(\mu\text{A h/cm}^{2}-\mu\text{m}\). The capacity loss of the initial charge-discharge was about 48\%, which may be associated with the fact that the formation of a solid-electrolyte interface (SEI) layer on the surface of the tin oxide.

4.2.4.2 Cylability

Figure 4-16 shows the discharge capacities vs. the number of charge/discharged cycle at a constant rate of 0.3 mA/cm\textsuperscript{2}. The cycling behavior shows a progressive “activation” of the sample. There is a slight increase in capacity with increasing cycle numbers. The initial specific capacity was about 352.8 \(\mu\text{A/cm}^{2}-\mu\text{m}\), and was gradually increased to a maximum value \(~490 \mu\text{A/cm}^{2}-\mu\text{m}\) after 20 cycles. The reversible capacity maintained at about 460 \(\mu\text{A/cm}^{2}-\mu\text{m}\) after 80 cycles at a charge/discharge rate of 0.3 mA/cm\textsuperscript{2}. The discharging capacity retention was about 93\%. 

88
Figure 4-16. Discharge capacities vs. the number of charge/discharge cycles for the nanostructured tin oxide thin film. The charge/discharge rate is 0.3 mA/cm².

Summarized in Table 4-2 are the electrochemical properties of SnO₂ thin films prepared by different method.\[34, 45, 48-49\] The reversible capacity of the nanostructured tin oxide film electrode prepared by combustion CVD is higher than those prepared by other methods. Moreover, the cyclability of this film electrode is also superior.
Table 4-2  Comparison of the capacities of various SnO\textsubscript{2} thin films (unit: μAh/cm\textsuperscript{2}-μm)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Preparation Method</th>
<th>Voltage range</th>
<th>Current density</th>
<th>Reversible capacity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO\textsubscript{2}</td>
<td>E-beam</td>
<td>0.1-0.8V</td>
<td>0.1 mA/cm\textsuperscript{2}</td>
<td>200 μAh/cm\textsuperscript{2}-μm</td>
<td>[45]</td>
</tr>
<tr>
<td>Si-SnO\textsubscript{2}</td>
<td>E-beam</td>
<td>0.1-0.8V</td>
<td>0.1 mA/cm\textsuperscript{2}</td>
<td>302 μAh/cm\textsuperscript{2}-μm</td>
<td>[45]</td>
</tr>
<tr>
<td>SnO\textsubscript{x}</td>
<td>Sputtering</td>
<td>0.01-1.4V</td>
<td>0.1 mA/cm\textsuperscript{2}</td>
<td>498.33 μAh/cm\textsuperscript{2}-μm</td>
<td>[58]</td>
</tr>
<tr>
<td>SnO\textsubscript{2}</td>
<td>Sputtering</td>
<td>0.1-1.1V</td>
<td>0.3 mA/cm\textsuperscript{2}</td>
<td>250 μAh/cm\textsuperscript{2}-μm</td>
<td>[59]</td>
</tr>
<tr>
<td>SnO\textsubscript{2}</td>
<td>Combustion CVD</td>
<td>0.1-1.0 V</td>
<td>0.3 mA/cm\textsuperscript{2}</td>
<td>352.77 μAh/cm\textsuperscript{2}-μm</td>
<td>This work</td>
</tr>
</tbody>
</table>

4.2.4.3 Rate Capability

Figure 4-17a shows the dQ/dV curves during charge (lithium insertion). And Figure 4-17b shows the dQ/dV curves during discharge (lithium desertion). In the first charging cycle, there are two peaks at 0.85 V and at 0.3 V respectively. Later, the peak at 0.3 V shifts to 0.25 V, and a peak at 0.12 V is clearly emerging. The dQ/dV curves during discharge are smooth. The peak centered at 0.45 V is wide. And there is another wide small peak around 0.6-0.8. As depicted by Dahn et. al \cite{33}, the peaks in the curves arise due to the coexistence between Li-Sn alloy phases of different composition. It was speculated that there is one-to-one correspondence between a dQ/dV profile of a given shape and a particular tin cluster size \cite{33}. However, more experiments are needed to verify this speculation.
Figure 4-17 Rates of lithium insertion and desertion (dQ/dV) as function of voltage for the nanostructured tin oxide thin film, a) during charge; and b) during discharge. The first, fifth, tenth and thirtieth cycles are shown.
Cycling tests were carried out at different current densities ranging from 0.3 to 0.9 mA/cm\(^2\) over a voltage range of 0.1-1 V. As shown in Figure 4-18, lower capacities were observed at increased discharge rate. For example, when discharged at a current density of 0.9 mA/cm\(^2\), the capacity retention obtained was about 64% of the capacity at the current density of 0.3 mA/cm\(^2\). It is worth to note that almost 100% capacity was retained when the charge/discharge rate was switched back to 0.3 mA/cm\(^2\) after tested at high rates for 60 cycles.

![Figure 4-18a](image1.png) ![Figure 4-18b](image2.png)

**Figure 4-18** a) Discharge capacity retention at different charge/discharge rate vs. the number of cycles for the nanostructured tin oxide thin film (continued after cycle test shown in Figure 4-16), b) Discharge capacity retention as discharge current density.

The high capacity and good cycleability are attributed to the unique columnar morphology of the films with subtle nanosized features. Firstly, the tin oxide electrodes fabricated by combustion CVD are highly open and porous. It appears that each SnO\(_2\)
grain grew on top of the gold coated Si substrate independently, with growth rate much faster in the direction normal to the substrate surface, forming columnar shape with wide, straight, and open voids between the grains. For porous films consisting of compacted nanoparticles, either poor inter-particle contact or the tortuosity may make some portion of the particle surface electrochemically inactive. The columnar configuration of the films prepared by combustion CVD enables most of the grain surface readily accessible to liquid electrolyte. Larger accessible surface areas would lower the current density; decrease the possibility of local destruction of structure due to large Li\(^+\) ion flux. Secondly, as shown in the inset of Figure 4-14b, the surface of columnar grains is covered by ultra fine particles of less than 20 nm. Fast surface lithium ion insertion-desertion interaction is expected. Thirdly, this is essentially a three-dimensional electrode configuration for lithium ion batteries. The longitudinal connectivity of electroactive materials throughout the film thickness offers additional advantage of fast electron/ion transport. The kinetic hindrance for lithium extraction depends not only on the Sn particle size, also on the architecture. Lithium transport is hindered by the slow transport kinetics of lithium from the bulk to the surface of the electroactive material particles. Fast transport kinetics would avoid ion depletion regions or concentration gradients that can degrade cell performance.\[^{50-51}\] Especially at high charge/discharge rates, large Li\(^+\) insertion or extraction fluxes at the surface and slow Li\(^+\) transport in the bulk result in concentration polarization of Li\(^+\) within the electrode material. The suitable ratio of surface area to thickness would improve cell performance. Moreover, the gaps between column grains not only provide easy access of the surfaces to liquid electrolyte, but also prevent agglomeration or growth of the grains, offering micro structural stability. Further,
the uniformly distributed thin Li$_2$O film could also help accommodate the mechanical stress resulted from the large volume change during alloying and de-alloying cycles to maintain the structure integrity.

4.2.5 Conclusions:

Three dimensional SnO$_2$ anodes with nanostructured columnar grains were fabricated using a combustion CVD method. The thickness was readily controlled by the deposition time, varying typically from 1 to 5 μm. The as-prepared films demonstrated good electrochemical performance. The maximum obtainable reversible specific capacity of the tin oxide film was about 490 μAh/cm$^2$-μm. More than 93% of the reversible capacity (460 μAh/cm$^2$-μm) was retained after 80 cycles at a current density of 0.3 mA/cm$^2$. More than 64% of the reversible capacity could be delivered at a discharge rate of 0.9 mA/cm$^2$. Combustion CVD has the potential to create unique electrode structures for high-performance lithium batteries.
4.3 Reference


5.1 Multi-scale Porous MIEC Electrodes Prepared by Breath Figures

5.1.1 Introduction

Solid oxide fuel cells (SOFCs) represent one of the cleanest, most efficient and versatile technologies for chemical-to-electrical energy conversion. It is believed that low-temperature SOFCs have the potential to greatly reduce the cost of the materials and cell fabrication in addition to improved reliability, portability, and operational life. However, the interfacial polarization resistances between electrolyte and electrodes increase dramatically as the operating temperature is reduced. Thus, the development of novel electrode materials and/or unique microstructure is one of the critical issues in development of new generation SOFCs. To date, several new electrode architectures have been developed in order to create durable, effective, and functionally graded electrode structures for intermediate or low-temperature SOFCs. Among these novel electrodes, multi-scale porous mixed ionic-electronic conductors (MIEC) are most attractive for SOFCs and catalysis. Since MIECs allow simultaneous transport of both ionic and electronic defects, the use of an MIEC as electrode may extend the active electrochemical reaction sites from the traditional triple-phase boundaries (TPBs) at the interface between an electronic conductor electrode and the electrolyte to the entire MIEC/gas interface, which can be orders of magnitude larger than the traditional TPBs, as schematically shown in Figure 5-1. The degree of this extension depends critically on
the rate of defect transport through the solid MIEC, gas transport through the pores to promote surface coverage in the MIEC, and the catalytic activity of interfaces. Gas transport through a porous electrode depends largely on the architecture of the electrode. Multi-scale porous MIECs are ideally suited for electrode applications: macro-pores (on the order of microns) promote rapid gas transport through the porous electrodes, nano-pores provide high surface areas for gas adsorption/desorption and for more catalytically active sites for electrode reactions. However, the creation of such a porous structure is yet to be achieved.

![Figure 5-1](image.png)

**Figure 5-1.** Schematic diagram of TPBs of a porous cathode only providing electrons (TPBs are located at the cathode/electrolyte interface) (left), and MIEC cathode transfers both electrons and oxygen vacancies (TPBs are extended to the surface of the MIEC) (right).

To date, a variety of templating methods that use self-assembly could create structures with submicrometer dimensions. Among them, recent developments using colloidal crystal templating allow the preparation of ordered macroporous materials that have three-dimensional ordering of pores with dimensions of tens to thousands of
The use of organic templates to control the structure of inorganic solids is proven very successful, especially in designing porous materials with pore sizes ranging from nano- to micrometers. For example, polymer spheres (PS) have been effectively used as template to create ordered macroporous oxides, carbon, and polymers with monodisperse, periodic voids in the 0.1-1 μm size range. These synthesis methods rely on filling or coating the void spaces between close-packed spheres with liquid metal alkoxides, resins, or gas phase precursors and subsequent precursor solidification in situ. Often, the collapse or loss of the 3D porous structure occurs during or after the template removal because of the fragile nature of the materials with a wall thickness much smaller than the pore size. Although methods for shaping and structuring certain solids into functional objects have been developed and improved to create increasingly more complex features, it is still a challenge to apply PS colloid template directly to the synthesis of macroporous MIEC electrode materials. First, the compositions of these electrodes are complicated. For example, a typical composite anode may consist of metallic Ni and Ce₀.₉Gd₀.₁O₁.₉₅ (GDC) whereas a typical cathode may consist of Sm₀.₅Sr₀.₅CoO₃ (SSC) and GDC. Thus, it is difficult to obtain the desired stoichiometry from solution containing more than one type of metal precursors using conventional templates. Second, the porous structure must have adequate thermal and mechanical stability during fabrication and operation. Often, it is difficult to retain the macroporous structure of the composite framework as the template is removed at high temperatures.

Here, a novel method to prepare multiscale porous MIEC electrode materials using polymer foam as the template, which is created by evaporating solution of polymer
in volatile solvents in a relative humid environment. Subsequently, a slurry consisted of
preformed MIEC nanoparticles is coated on the template. After thermal decomposition of
the organic template, porous MIEC electrode materials remain.

5.1.2 Experimental

5.1.2.1 Preparation of Multi-scale Porous MIEC

Synthesis of PMMA colloid: Monodisperse PMMA spheres were synthesized
using an surfactant-free emulsion procedure which was described in literature. Typically, 15 wt.% methyl methacrylate, 84.88 wt.% distilled water are placed into 3-necked rounded bottom flask. The system is under moderate stirring and kept at 80 °C for 30 minutes to attain temperature equilibrium. Then, a specific amount of the initiator, 0.12 wt.% 2,2′-Azobis(2-methylpropionamide) dihydrochloride is added. The reaction is sustained at 80 °C for another 3 hours and then cooled to room temperature. The close-packed PMMA spheres were obtained by centrifugation and dried under ambient condition for one week.

Preparation of MIEC materials: Nanocrystal Ce$_{0.9}$Gd$_{0.1}$O$_2$ (GDC) powder,
Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ (SSC) powder and NiO powders were prepared using a glycine-nitrate process (GNP) which is described in detail elsewhere. The stoichiometric amounts of precursors (NH$_4$)$_2$Ce(NO$_3$)$_6$, Gd(NO$_3$)$_3$·6H$_2$O (99.9%) were dissolved in 40mL distilled water to form 0.5 M aqueous solution, to which glycine was then added in solid state. The molar ratio of NO$_3^-$ to glycine was kept at 2. The resulting solution was then heated to evaporate the excess solvent on a hot plate, and the residual viscous resin transformed to brownish-dark foam. When further heated, it ignited, yielding a voluminous, yellow, sponge-like ash. NiO and SSC powders were prepared with a similar
procedure. The as-prepared GDC, SSC and NiO ashes were subsequently fired at 600°C, 800°C, and 850°C, respectively.

*Preparation of slurries:* Proportional amounts with the weight ratio 1:1:2 of SSC and GDC powders, V006 binder and acetone were mixed together by ball mill for at least 24 hours. The ratio of electronic conductor SSC to ionic conductor GDC powders was 7:3 by weight. The slurry for the anode consisting of 65%wt. NiO and 35% GDC was prepared in a similar manner. [15-16]

*Film formation (shown in Figure 5-2):* Synthetic close-packed PMMA spheres were crushed into powders which were subsequently dispersed in ethanol/ turpentine (from Heraeus)(10 vol%)/xylenes(10 vol%). The concentration is ranging from 5~9% by weight. The PMMA suspension was dropped and spread on the surface of the YSZ or GDC pellet. And the polymer film was dried at ambient atmosphere for two hours (humidity 65%). Then the slurry was diluted by ethanol and drop-cast on the top of the template by using small syringes. As the solvent was imbibed into the interstices of the polymer foams, the nanocrystals of the composites in the slurry were also imbibed into the interstices and coated on the foams. The coated sample first sat at ambient atmosphere for 1 hour, and then was heated and held at 60°C for 2hrs, and finally underwent thermal decomposition of organic template. The samples were calcined in air first at 350°C for 3hrs, and then fired at 550°C for 5hrs with a heating rate 2°C/min. Some of the samples were subsequently fired at 800°C for 2hrs. The PMMA foam and binder were decomposed during calcinations, yielding dual scale porous MIEC thin film.
Figure 5-2. Schematic of the electrode processing to form multi-scale porous electrodes. (a-b) A polymer film with uniform array of pores (“air bubbles”) could be formed by a moisture casting process: spreading a layer of dilute polymer solution in a volatile solvent on an electrolyte substrate and subsequent solvent evaporating under moisture [17]. (c) Slurry coating of prepared MIEC nanocomposites and (d) burning off of the polymer film and binder.
5.1.2.2 Characterization of Multi-scale Porous MIEC

X-ray powder diffraction (XRD) patterns were acquired on a Philips PW-1800 X-Ray Diffractometry with CuKα radiation. N₂ adsorption measurements were performed at 77K with a Micromeritics ASAP 2000 system. The samples were degassed at 300°C for 4 h. SEM images were obtained using a Hitachi S-800 Scanning Electron Microscope. Impedance measurement were performed at temperature range 650~800°C, in the frequency range from 0.01Hz to 100 KHz with a lock-in amplifier (model 5210) and an EG&G potentiostat/galvanostat (model 273A) interfaced with a computer. The button cell configuration is SSC-GDC/(Bi₂O₃)₀.₇₅(Y₂O₃)₀.₂₅/Pt..

5.1.3 Microscopic Properties

5.1.3.1 Morphology of PMMA spheres

Shown in the Figure 5-3 are the synthetic PMMA spheres prepared by an emulsion polymerization of methyl methacrylate (MMA) in water. The experimental conditions such as the ratio of monomer concentration, initiator concentration and reaction temperature were varied to control the PMMA colloid size. The spheres with diameter between 310 nm and 570 nm can be obtained.
Figure 5-3 SEM images of PMMA spheres prepared by surfactant-free emulsion polymerization. The particle sizes are a) 310 nm, b) 430 nm, and c) 570 nm.

5.1.3.2 Morphology of Multi-scale Porous MIEC thin film
The PMMA spheres are suspended in ethanol/turpentine/xylenes mixtures. A film of PMMA foam is readily formed upon spreading several drops of the PMMA suspension onto the YSZ substrate in ambient atmosphere (humidity 65%). The ethanol, turpentine and xylenes were evaporated during the subsequent exposure at room temperature, leaving behind a foam-like film, as shown in Figure 5-4a. The size of the holes is about 1 μm. A slurry containing nanoparticles of MIEC composite precursors penetrated into the void space within the foam skeleton, coated the surface of the template, forming the pre-arranged skeleton for porous composite after solvent volatized, as shown in Figure 5-4b. Subsequent calcination at 500°C left the porous microstructure of MIEC composite (Figure 5-4c). The regularly and homogenously distributed cellular pores are of 0.8~1.5 μm in diameter. The void spaces were interconnected in three dimensions through walls of approximately 0.5~1 μm thickness. Figure 5-4d is an enlarged view of the Figure 5-4c. As we further investigate the microscopic feature of the wall as shown in the insert of Figure 5-4d, the pore walls are built from nanoparticles with an average diameter of about 100nm. The voids between these particles form a continuous and nanoporous wall structure. In this way dual porosity (macro- and mesopores) is induced.
Figure 5-4. SEM images of (a) foamy PMMA film, (b) as prepared green structure of foamy PMMA after infiltrated with SSC-GDC slurry, and (c-d) porous SSC-GDC electrode materials after fired at 550°C for 5hrs (insert is the enlargement of the wall composed of MIEC nanoparticles)
5.1.4 Nitrogen Adsorption: Surface Area and Pore Size Analysis

The Brunauer-Emmett-Teller (BET) surface area and the pore volume were estimated using N$_2$ adsorption measurements on samples degassed for 4 h at 300°C. The specific surface area of the porous structure as determined using the BET method is about 19 m$^2$g$^{-1}$. Shown in Figure 5-5 is the pore-size distribution, as calculated using BJH (Barrett-Joyner-Halender) theory from the N$_2$ desorption data. The two peaks centered around 2.5 and 35 nm indicate that the walls of the cells are also mesoporous and a combined meso-/macroporous structure was created.

![Nitrogen adsorption-desorption isotherms for a porous GDC-SSC materials calcined in air at 800°C for 2 hours.](image-url)

Figure 5-5  Nitrogen adsorption-desorption isotherms for a porous GDC-SSC materials calcined in air at 800°C for 2 hours.
5.1.5 Thermogravimetric Analysis

Figure 5–7 showed the TGA experiments on the calcination of the polymer foam/MIEC composites. The absorbed water started to evaporate above 100°C and appears to have been completely lost at about 250°C, where the only remaining components were the PMMA foam, V006 binder and MIEC (30%wt. GDC+SSC). Hence, the weight of the sample was normalized to 100% at 250°C. The sample started losing weight rapidly above 250°C, presumably as a result of the thermal degradation and evaporation of the PMMA and the binder. The PMMA foams were totally decomposed and evaporated by 340°C. The remaining weight of about 39.8% may be attributed to the GDC+SSC. The weight loss of approximately 40% is attributed to the burning off polymer template and V006 binder. The weight ratio of V006 and GDC+SSC in the slurry is 1 to 1. Then about 39.8% of the total weight loss is attributed to the V006 binder.

Figure 5-6 BJH pore size distribution for a porous GDC-SSC materials calcined in air at 800°C for 2 hours.
Only 20.2% of the total weight loss is attributed to the PMMA polymer. If only PMMA polymer and GDC+SSC are considered, the weight concentrations of these two components are normalized as 33.67% for PMMA, and 66.33% for GDC+SSC.

Figure 5-7. (a-b) TGA curves for MIEC materials (30wt.% GDC+SSC) from polymer foam. (b) TG curves with normalized weight loss at 250°C.
An estimated of the porosity of the final material can be determined to be 76.77% according to the Equation (5-1).

\[
\text{impurity volume}\% = \frac{f_{\text{imp}}}{\frac{f_{\text{imp}}}{\rho_{\text{imp}}} + \frac{1 - f_{\text{imp}}}{\rho_{\text{solid}}}}
\]  

(5-1)

Where \(\rho_{\text{imp}}\) is the density of the impurity, \(f_{\text{imp}}\) is the weight fraction of the impurity or the TGA weight loss due to impurity, and \(\rho_{\text{solid}}\) is the bulk density of remaining solid.

\[
\text{pore volume}\% = \frac{33.67\%}{\frac{33.67\%}{1.06 \text{ g/cm}^3} + \frac{66.33\%}{6.9 \text{ g/cm}^3}} \times 100\% = 76.77\%
\]

5.1.6 Formation Mechanism

“Breath figures” represents the vapor condensation patterns that are formed on cold surfaces.[18] Beysens et al has studied the phenomena of water droplets condensation on cold solid surfaces.[19] And it is well-known that evaporation of volatile organic liquids can lead to condensation of water droplets in the sub-micrometer size range.[20-21] Solvent evaporation decreases the air-liquid interfacial temperature. If the temperature falls below the dew point, water droplets condense on the surface. Ethanol, turpentine and xylene are relatively volatile. The high vapor pressure of the solvents drives solvents evaporation, and rapidly cools the surface. This cooling leads to the condensation of water droplets on the evaporating surface. They grow and interact. The interaction between droplets, coupled with convective currents in the evaporating solvents drive the self-assembly of the packing of the water droplets.[19-23] When solvents are less dense
than water, the porous array will propagate through the film,\textsuperscript{[20]} and 3D array is produced. The obtained morphologies present very regular and homogenous pore structures. Instead, the morphologies obtained from templating of single colloidal crystal sphere have a characteristic feature of monodisperse and periodic pore structure. Hence, in this study, it is this polymeric superstructure that act as template, instead of the direct templating of single polymer sphere.

5.1.7 Microstructure Comparison

Figure 5-8 shows the SEM images of a dual scale porous electrode, composed of a continuous network of SSC and 30wt.%GDC MIEC composite, after the removal of the template by firing at 800°C. The porous array of submicron-sized holes extends over a range of thousands of micrometers on the substrate (Figure 5-8a). As shown in Figure 5-8b, the electrode consisted of regularly distributed cellular pores of 1 $\mu$m in diameter. The interconnected walls are approximately 0.5~1 $\mu$m thick. The primary particles of the composite are about 100 nm. It is noted that, the wall of the network is nanoporous due to the burn off of the organic binder in the slurry, which is idea structure for a SOFC cathode compared to the structure shown in Figure 5-8c without template. The micron interconnected pores facilitate fast gas diffusion and mass transport, while the nanoporous walls consisted of MIEC greatly extend the TPBs, and shorten the transport path.
Figure 5-8. Microstructures (SEM photographs) of (a-b) interconnected porous SSC-GDC MIEC cathode fired at 800°C for 2hrs (insert shows the nanostructure of porous wall area); and (c) SSC-GDC MIEC cathode prepared by slurry coating without template.
Changes of the templated morphologies can occur in conventional templating approaches, as significant shrinkage \cite{6,7} and crystal growth are often observed. \cite{7} To date, only one paper reported successful synthesis of ordered macroporous SSC. \cite{2} In the present method, the fired temperature has less effect on the pore size and particle size. The pore size fired at 800°C is almost the same as that fired at 550°C, which is about 1 μm. And the wall is still about 0.5~1 μm. This is because that, firstly, there is less room for the precursor to shrink as the polymer spheres are being removed because the precursor is made of solid suspension instead of liquid solution. Secondly, there is much less shrinkage due to the particle growth because the SSC and GDC powders are pre-heated treated at high temperature, as it is shown in the inserted figure, there is no sign of significant grain growth. Third, the wall is comparatively thick and strong enough to support the whole structure after removal of template. Compared to conventional polymer sphere templating process, thicker pore walls with mechanically more stable materials were obtained due to the templating of the polymeric superstructure instead of single spheres.

Furthermore, the desired stoichiometric composition had been assured before the infiltration. Figure 5-9 shows the XRD patterns of prepared MIECs, implying that the films are composed of desired phase, SSC and GDC.
5.1.8 Electrochemical Properties of Multi-scale Porous MIEC

The cell configuration is SSC-GDC/(Bi₂O₃)₀.₇₅(Y₂O₃)₀.₂₅/Pt. Figure 5-10 presents the Arrhenius plots of SSC-GDC cathode/electrolyte interfacial polarization resistance. The activation energy was calculated as 130 kJ/mol. At 750°C, the cathodic interfacial resistance is as low as 0.39 Ωcm², implying that the porous cathode is promising for the use in the intermediate-temperature SOFCs. The performance of cathode is sensitive to processing, which determine the microstructure and adhesion of the electrode to the
electrolyte. During operation, we found that the adhesion between electrode/electrolyte is needed to be improved to get better performance.

Figure 5-10. (a) Impedance spectra of a cell with configuration of SSC-GDC/(Bi2O3)1.75(Y2O3)0.25/Pt. (b-c) The cathodic polarization resistances, $R_p$, of the interface between porous GDC-SSC and a dense (Bi$_2$O$_3$)$_{1.75}$(Y$_2$O$_3$)$_{0.25}$ electrolyte as determined from impedance spectra acquired at different temperature.
One of the biggest advantages of this method is the ability to control easily the dimensions and distribution of resulted pores by varying the pore size of the invert opal structure of the template by breath figures. The methodology of this templating process appears to be extendable readily to other electrode materials, as long as the size of the precursor particles is in the nanosize range. For example, porous anode consisting of NiO and GDC was obtained using the same process followed by firing at 800°C (Figure 5-11). The NiO-GDC composite was verified by the XRD pattern (Figure 5-12). Large regions of regular and homogeneous holes with diameter about 1 \( \mu \text{m} \) were formed under same conditions. The wall is also porous and about 1 \( \mu \text{m} \) thick. The average primary particle size is about 100 nm.

Figure 5-11. (a-b) SEM photograph of dual scale porous NiO-GDC anode film fired at 800°C for 2hrs (insert shows the nanostructure of porous wall in white block).
We also tried to form YSB-AgO MIEC. However, the precursor particles are too large to filtrate into the whole skeleton and to obtain a continuous coverage of the coating over the scalford. After calcination at 500°C, the scaffold was burnt away and a discontinuous YSB-AgO MIEC left.

**5.1.9 Conclusions**

In summary, the preparation and characterization of novel, regular, homogeneous and dual porous MIEC materials for electrodes of SOFCs have been described. Foam-like thin film templates form upon evaporation of volatile solvents that induces water
condensation from a relatively humid environment. The template is used to direct the porous structure of MIEC materials. After removal of the organic template by calcination, the resulted SSC-GDC, and NiO-GDC composite electrodes retained their macroscopic shapes. The macropores promote rapid gas transport through the porous electrodes, mesoporous provide high surface areas for gas adsorption/desorption and more catalytically active sites for electrode reactions. Electrochemical characterization was performed using EIS. The cathodic interfacial resistance is as low as $0.39 \, \Omega \text{cm}^2$ at $750^\circ\text{C}$, implying that the porous cathode is promising for the use in the intermediate-temperature SOFCs. It provides a promising way to synthesize dual scale porous electrodes for solid oxide fuel cells.
5.2 Synthesis of Porous GDC-LSM MIEC Cathodes by Sol-gel

5.2.1 Introduction

It is well known that cost reduction is one of the major challenges facing the current solid oxide fuel cell (SOFC) technologies. To dramatically reduce the cost of materials, the operating temperature must be reduced; to reduce the cost of fabrication, new design and fabrication processes must be developed. Recently, we have developed a very unique process for fabrication of honeycomb fuel cells with built-in interconnection and gas manifolding.\textsuperscript{[24]} However, one difficulty in achieving high-performance is how to fabricate efficient electrodes on extruded honeycomb cells, where the fabrication methods are essentially limited to solution/slurry coating techniques.

LaMnO$_3$-based perovskites exhibit intrinsic p-type conductivity due to changes in the Mn valence. The electrical conductivity of these materials is greater than 10 S cm$^{-1}$ at 700°C. The electric conductivity is enhanced by replacing La$^{3+}$ with lower valence cations (such as Ca$^{2+}$, Sr$^{2+}$) or doping with other cations (Mg$^{2+}$, Co$^{3+}$, etc) for application as a cathode material.

In particular, strontium-doped lanthanum manganite (LSM) is known to be a classical cathode for SOFCs due to its thermal expansion and chemical properties compatible with stabilized zirconia. Composite electrodes consisting of LSM and the electrolyte materials such as yttria stabilized zirconia (YSZ) and gadolinia doped ceria (GDC) are proven to have better performance than electrodes consisting of LSM alone, due to possible mixed conductions and the presence of active triple phase boundary (TPB) between LSM, electrolyte, and gas phase in the bulk of the electrode.\textsuperscript{[25-26]} Furthermore, the performance of an LSM cathode is sensitive to processing, which...
determine the microstructure and the adhesion of the electrode to the electrolyte, and thus
determine the length of the triple phase boundary (TPB). The TPBs are believed to be the
most active sites for oxygen reduction in the electrode [27-28].

Various methods have been used for the fabrication of LSM cathodes, including
slurry coating, flame spraying, tape calendaring, casting, and printing [24]. LSM and
LSM-based composite films have also been fabricated by electroless deposition [29],
electrochemical deposition [30], vacuum evaporation [31], metal-organic chemical vapor
deposition [32], metal-organic decomposition [33], vacuum plasma spraying [34], and screen-
printing [35]. However, little work has been aimed to develop a composite film of LSM-
YSZ or LSM-GDC on honeycomb SOFCs. In this letter, we report our finding on LSM-
GDC composite films prepared using a sol-gel process as cathodes for SOFCs with
honeycomb structures. The electrodes show much smaller interfacial polarization
resistances than those prepared by other methods such as slurry coating 26,36 or spray
deposition 37.

5.2.2 Experimental

5.2.2.1 Preparation of GDC-LSM

Gd$_{0.1}$Ce$_{0.9}$O$_{1.95}$ (GDC) sol was prepared from (NH$_4$)$_2$Ce(NO$_3$)$_6$ and Gd(NO$_3$)$_3$. The
nitrates were added dropwise into ammonia solution (pH>11) to form hydroxide
precipitates (pale yellow in color), which were then peptized with nitric acid (to pH 3.5)
at 85°C to form a clear GDC sol. (La$_{0.85}$Sr$_{0.15}$)$_{0.9}$MnO$_{3+\delta}$ (LSM) powder was prepared
using a glycine-nitrate process with precursors of La(NO$_3$)$_3$, Sr(NO$_3$)$_3$, Mn(NO$_3$)$_2$, and
glycine 36. The powder was fired at 800°C for 4 hrs to form the perovskite structure as
confirmed by X-ray diffraction (PW 1800). The fired powder was subsequently dispersed
into the GDC sol with ball mill to form a slurry-like sol, in which the weight ratio of GDC to LSM was 1:1. The sol was subsequently coated onto the inner channels of YSZ (8% mole yttria stabilized zirconia) honeycombs, which were fabricated by extrusion and sintering at 1350°C in air for 12 hours [24]. The coated layer was dried at room temperature and fired at 600°C for 2 hours with a heating and cooling rate of 1°C and 5°C per minute, respectively. The coating-drying-firing procedure was repeated 10 times before impedance measurements.

Figure 5-13 Schematic of the electroding process on honeycomb electrolyte.
5.2.2.2 Characterization

The microstructures of the cells were revealed using a scanning electron microscope (SEM, Hitachi S800). A layer of the electrode materials, deposited on a dense alumina substrate using the identical processing procedures, was then used for transmission electron microscopy, X-ray diffraction, and isothermal nitrogen adsorption-desorption (BET) measurements.

Electrochemical impedance measurements were performed on symmetrical cells, LSM-GDC/GDC/LSM-GDC, in air with the LSM-GDC composite electrodes being finally fired at 800°C for 4 hours or without further firing (in-situ testing) using a Solartron 1255 HF frequency response analyzer in combination with a Solartron 1286 electrochemical interface. Silver wires were attached to the electrodes with a silver paste, and a thermocouple was positioned close to the sample to provide an accurate measurement of the sample temperature, usually increasing from 500 to 750°C in 50°C interval. Impedance spectra were obtained in the frequency range from 10 mHz to 1 MHz with an applied ac voltage amplitude of 10 mV. All impedance measurements were taken 30 minutes after the desired temperature was reached under open circuit conditions.

5.2.3 Microscopic Properties

Figure 5-14 shows a typical cross-sectional view (SEM image) of an LSM-GDC cathode (about 10μm thick) fired at 800°C, which appears to be well adhered to the electrolyte. The LSM and GDC grains appear to bond together and there is a high level of interconnected porosity. The average grain size (estimated from SEM micrographs) appears to be about 100 nm. However, the BET measurement indicates that the specific area of the cathode fired at 800°C is about 8.6 m²/g, which implied an average grain size
of about 50 nm. TEM observation (Figure 5-15) shows that these grains are consisted of much smaller particles, with dimension of about 10 nm.

Figure 5-14. A cross-sectional view (SEM) of a GDC-LSM composite cathode fired at 800°C for 4 hours.

Figure 5-15. (a-b) TEM image of the GDC-LSM composite cathode fired at 800°C for 4 hours.
Shown in Figure 5-16 are the XRD patterns of the composite powder prepared by the sol-gel process, GDC by the sol-gel process, and LSM by a glycine-nitrate process, suggesting that no chemical reaction between GDC and LSM has been developed during the sol-gel process or the subsequent firing of the composite at 1000°C for 4 hrs. High stability is thus expected for the sol gel derived cathodes that is processed at temperature below 800°C.

Figure 5-16. The XRD pattern of a composite GDC-LSM powder prepared with a sol-gel process and fired at 1000°C for 2 hours (the XRD patterns of LSM and GDC fabricated with a glycine-nitrate process and a sol-gel method, respectively, are also shown for comparison).
5.2.4 Electrochemical Properties

Shown in Figure 5-17 is a typical impedance spectrum for a symmetric cell, LSM-GDC/YSZ/LSM-GDC, as measured at 700°C in air. The spectrum consists of an arc at low frequencies (0.01-10 Hz) and an arc at high frequencies (10-10000Hz). The spectra obtained at different temperatures are very similar, each consisting of two well-separated arcs. While any attempt to deduce oxygen reduction mechanism or even to separate the contributions from mass transfer and charge transfer requires other independent measurements, it is straightforward to determine the total interfacial polarization resistances of the symmetrical cell (2 Rp as marked on Figure 5-16) directly from this impedance spectrum.[26] To obtain the actual polarization resistance in \( \Omega \text{ cm}^2 \), however, the total interfacial polarization resistances should be corrected for electrode area and divided by two\(^{[38-39]} \). This is because the total interfacial impedance of a symmetrical cell corresponds to that for two identical electrode-electrolyte interfaces of the cell. Further, the interfacial processes occurring in the symmetrical cell under the conditions for impedance measurements are identical to those occurring at the cathode-electrolyte interface of an SOFC such as air, LSM-GDC/GDC/Ni-GDC, hydrogen under impedance measurement at open circuit conditions. Since the purpose of this study is to characterize the effect of microstructure (or active surface area) on interfacial polarization resistance of the same electrode material, the polarization behavior of the electrodes under different DC voltages were not studied. In fact, the interfacial impedance responses under open circuit conditions represent the equilibrium properties of the interface and, thus, are related to the exchange current densities or catalytic
properties of the interface. We believe that the interfacial polarization resistance is the most critical parameter for this study while the cathodic and anodic transfer number should be less sensitive to change in microstructure.

Figure 5-17. A typical impedance spectrum for a symmetric cell, GDC-LSM/YSZ/GDC-LSM, as measured at 700°C in air. The polarization resistance of the electrode (LSM-GDC) and the electrolyte (YSZ) interface, Rp, was determined directly from this impedance spectrum.

Shown in Figure 5-18 is the temperature dependence of interfacial polarization resistances measured under open circuit conditions for the sol-gel derived cathodes with microstructures shown in Figure 5-13. The interfacial resistances of the composite cathodes (GDC-LSM [26]), and recently developed functionally graded cathodes [36-37] consisting of GDC and LSM are also shown in Figure 5-17 for comparison. It is clear that the sol-gel derived cathode displayed much better electrochemical performance than the other cathodes, although they all have the same chemical composition. For example, at
700°C, the interfacial resistance of a sol-gel derived cathode is only 0.28 Ωcm², compared to 4.3 Ωcm² of a graded cathode [36], and 6.8 Ωcm² of a slurry-coated GDC-LSM composite [26].

![Figure 5-18 Interfacial polarization resistances of LSM-GDC electrodes (on an YSZ electrolyte) prepared by different processes: a sol-gel process as reported in this work, a slurry coating [36], a spin coating [26], and a spray coating [37] process.](image)

The interfacial polarization resistances depend critically on electrode microstructure; high porosity, small grains, and large specific surface area results in low
interfacial resistances. The average grain size of the sol-gel derived cathode is about 0.05 μm, smaller than that of glycine-nitrate derived cathode (0.1–0.2 μm) \[^{[36]}\], and much smaller than that of the commercial available particles (2–3 μm) as used for the composite cathode \[^{[26]}\] and graded cathode \[^{[37]}\].

The interfacial resistances are very sensitive to the firing temperatures as well. When firing temperature of the electrode is too high, the interfacial resistances increase with the firing temperature due to over-sintering of electrodes, leading to loss of porosity, surface area, and active triple-phase boundaries. On the other hand, when the firing temperature is too low, the bonding between the electrode and electrolyte is too poor, resulting in high interfacial resistances. For the commercially available and glycine-nitrate derived LSM-GDC powders, the lowest sintering temperatures are 1125 and 1050°C \[^{[36-37]}\], respectively. It is generally believed that films fabricated by a sol-gel process have strong bonding with the substrate even the firing temperature is relatively low. A cell with cathode sintered in-situ at 600°C behaves in a similar manner as a function of temperature as the cell with cathode fired at 800°C. For example, the interfacial resistance of an in-situ fired electrode is 3.3 Ωcm\(^2\) at 550°C (comparing to 3.5 Ωcm\(^2\)), and 0.11 Ωcm\(^2\) at 800°C (0.12 Ωcm\(^2\)). This implies that adequate bonding has been formed between the electrolyte and electrode at temperature as low as 600°C. This is especially important to SOFCs to be operated at low temperatures.

Moreover, in my point of view, when the particle size was as small as 10 nm, the semi-infinite boundary condition was not satisfied any longer. Hence the nanosize effects including mesoscopic overlapping of the space charge took place. In the view of extrinsic-intrinsic transition of the pure materials, two main factors would be considered for reducing interfacial polarization resistance. One is TPB effect. The other is nanosize
effects. When the particle size satisfies the semi-infinite boundary condition, TPBs have an important effect on the electrode kinetics. The TPBs can be increased by increasing porosity and decreasing particle size, i.e. increasing surface-volume ratio. Nanosize effects would take place when the particle size is so small that the semi-infinite boundary condition and the charge-neutrality in the bulk of the particle are no longer invalid. The overlapping of the space-charge would greatly influence the ionic conductivity, electronic conductivity and surface catalytic properties. However, the conclusive proof of this effect is still lacking. This is subject to future work which is described in the future work part (Chapter 7).

5.2.5 Conclusion:

Highly porous cathodes consisting of LSM and GDC with low interfacial polarization resistances have been successfully fabricated by a sol-gel process, which has the advantage of developing strong bonding between the electrode and electrolyte at low temperatures and achieving desirable microstructures for fuel cell electrodes: small grains, high porosity, large surface area, and long triple-phase boundaries. Moreover, the mesoscopic regime of overlapping space charge effects had a positive effect on the electrode kinetics.
5.3 Reference


CHAPTER 6
SELF-ASSEMBLY OF CERIUM COMPOUND NANOPETALS

6.1 Introduction

Ceria and ceria-based materials have received wide attention for various applications such as fast ion conductors (solid electrolytes as well as composite electrodes for intermediate temperature solid-oxide fuel cells),\textsuperscript{1,2} catalytic supports for automotive exhaust systems and for low-cost H\(_2\) generation in fuel cells\textsuperscript{3-6}, low-temperature (<600\(^\circ\)C) oxygen sensors and oxygen storage capacitors. The high oxygen storage capacity (OSC) in conjunction with special redox properties (involving lattice oxygen/oxygen vacancy participation) can catalyze CO oxidation on the CeO\(_2\) surface, making this system particularly useful in three-way catalysts for the treatment of automotive exhaust gas (hydrocarbons, CO and nitrogen oxides)\textsuperscript{5-6}.

Nanostructured materials have generated a lot of interest due to their unique physical and chemical properties. This is because many properties of materials, such as catalytic activity, sensitivity, or conductivity, are closely related to surface area and particle size. Preparation and controlled fabrication of ceria-based nanostructured materials with functional properties have attracted more and more attention. Masui et al.\textsuperscript{7} have synthesized ultrafine ceria nanoparticles with diameters of 2.6 nm for CO oxidation. Mesoporous ceria has been synthesized using a templating method.\textsuperscript{8} Cerium compound nanowires and nanorings have been obtained based on the direct-template method by AOT(bis(2-ethylhexyl) sulfosuccinate) anions and alkyl alcohols.\textsuperscript{9} Furthermore, nanosized ceria can be synthesized from the thermal decomposition of cerium compounds, such as cerium carbonates or hydroxycarbonates.\textsuperscript{10-12} Most previously
reported work on nanostructured ceria focused on the synthesis and properties of spherical ceria nanoparticles. In this work, we report for the first time the self-assembly of a new nanostructure, microsized nanopetals of cerium compounds, by a selected hydrothermal method using a mixture of water and ethanol as a reaction medium. The effects of solvent and concentration of the precursors on the resultant phases and morphologies were investigated and discussed. A mechanism is proposed to account for the formation of the phases and the nanostructures. The catalytic properties of different nanostructures towards CO oxidation were studied using Raman spectroscopy.

6.2 Experimental

6.2.1 Synthesis of Nanopellet Cerium Compound

Cerium ammonia nitrate was dissolved in distilled water. The molar ratio of water to Ce\(^{4+}\) ions ranged from 20 to 100. The solution was then added into ethanol while stirring (volumetric ratio of ethanol to water was 10:1). The resulting solution with a grape wine color was then transferred into a Teflon-lined steel autoclave and heated at 180°C for 10 h in an electric oven. The autoclave was then quenched to room temperature. The precipitates were collected, washed by distilled water and ethanol, and dried in an oven at 80°C. Some of the precipitates were subsequently calcined in air at 500°C for 5h or 800°C for 2h.

6.2.2 Characterization

The crystalline phase identification was performed through powder X-ray diffraction (XRD, PW 1800) using CuK\(\alpha\) radiation. The morphology and size of the precipitates were examined using a scanning electron microscope (SEM, LEO 1530) and
a transmission electron microscope (TEM, JEOL 100C). Most samples for SEM observation were sputtered with gold, except for the one used to determine the thickness of the nanopetals. N2 adsorption measurements were performed at 77K with a Micromeritics ASAP 2000 system to measure specific surface area.

For the Raman spectroscopy measurements, a Renishaw RM-1000 Raman microscope was used with an Ar ion laser excitation source tuned to 488 nm. The samples were 10 mm diameter pellets that had been pressed under 1 ton from 100 mg of either nanopetal ceria powders calcined at 500°C for 5h or spherical ceria nanoparticles (no calcination). The pellet was then placed into a temperature- and atmosphere-controlled Raman sample chamber (special order, Harrick Scientific). The pellet was pretreated at 50°C in vacuum (10⁻¹ Pa) for one hour before the adsorption experiment. A Raman spectrum of the pellet surface was then taken after exposure to a 10% O₂ (balance argon) atmosphere for 15 minutes. The pellet surface was then exposed to 10% CH₄ (balance argon) for 20 min before another spectrum was collected. Finally the pellet was reexposed to a 10% O₂ atmosphere. All gas flows were held at 100 ccm. Each Raman spectrum presented consists of 10 20-second spectra added together, giving a total exposure time of 200 seconds. The presence of any new peaks due to oxygen-containing species was confirmed using standard ¹⁸O₂/¹⁶O₂ isotope exchange methods.

6.3 Microscopic Features and Phase Structure of Cerium Compounds

6.3.1 Microscopic Features and Phase Structure of Nanopetlet Cerium Compound

Shown in Figure 6-1 are the XRD patterns of as-synthesized cerium compound nanostructure and those obtained after calcination at 500°C. The XRD pattern in Figure 6-1a indicated that the as-synthesized cerium compound can be indexed as a mixture of
hexagonal cerium carbonate hydroxide Ce(OH)CO₃ \((a=7.2382 \text{ Å} \text{ and } c=9.9596 \text{ Å}, \text{ JCPDS card No. 32-0189)}\) with a small amount of the cubic fluorite cerium oxide \((a=5.41134 \text{ Å}, \text{ JCPDS card No. 43-1002)}\). The XRD spectrum from the as-synthesized sample shows a textured structure compared with the XRD spectrum acquired from the standard hexagonal cerium carbonate hydroxide powders (Figure 6-1a). The strongest peaks in Figure 6-1b are \{11-20\} and \{30-30\}.

![XRD spectra](image)

**Figure 6-1.** (a) The standard XRD pattern of hexagonal Ce(OH)CO₃, (b) the as-grown cerium compounds with precursor ratio of Ce⁴⁺ to H₂O at 1:20, (c) fired samples at 500°C for 5h.

Figure 6-2 shows typical SEM images of the as-grown cerium compound with flower-like microstructures. The obtained micro-flowers varied in size from several
microns to several tens of micrometers (Figure 6-2a), and are assemblies of tens to hundreds of nanopetals (Figure 6-2b). From the top view and side view of the cerium compound nanopetals, the nanopetals stack layer by layer, tending to align along some orientation, looking like blooming flowers. The nanopetals are slightly curved, several microns in width, and approximately 10 nm in thickness (Figure 6-2c).

Figure 6-2. SEM images of as-grown cerium compounds with microflower shape under hydrothermal conditions at 180°C (molar ratio of Ce⁴⁺ to H₂O =1:20). (a)-(b) Ce(OH)CO₃ micro-flower at different magnifications, (c) top view of nanopetals, (d) side view of the nanopetals, (e) enlarged view of nanopetals without gold coating.
Shown in Figure 6-3 is a TEM bright-field image of cerium compound petals and the corresponding SAED pattern. The diffraction pattern is well-indexed as (0001) zone spots with $a=7.2382$ Å. The diffraction pattern indicates that these nanopetals have a “single crystalline” textured orientation and the side surfaces are {11-20} and {30-30} planes, in agreement with XRD results. This indicates that the growth velocity of the cerium compound nanopetal that is normal to the [0001] direction is much faster than that along the [0001] direction. The extra faded ring diffraction pattern could be indexed as ceria with cubic fluorite structure.

**Figure 6-3.** (a) TEM images of cerium compound nanopetals, (b) selected-area electron diffraction (SAED) pattern of the nanopetals in (a). The spot pattern is indexed as Ce(OH)CO$_3$ nanopetals. They have textured orientation along [0001]. The shaded ring pattern is indexed as ceria.
The specific areas for different calcinations temperature were measured. The results are 88, 97 and 36 m$^2$/g for the as-synthesized samples, the samples calcined at 500°C and those calcined at 800°C respectively. These results show the separated nanopetals were not easily sintered due to their unique structure.

6.3.2 Effect of the Ion Concentration on the Morphologies and Phases

The composition and morphology of the final product can be controlled by the cerium source, the cosolvent, and the relative concentration of metal ion and water. In this work, the precursor concentration in a mixed water-ethanol medium plays a key role in the synthesis of cerium compound nanopetals. A suitable concentration value can effectively prevent cerium ammonia nitrate hydrolysis to cerium oxide in the initial stage and kinetically control the growth of the nanostructures. When the molar ratio of water to metal ion is below 20, the product is mainly the cerium carbonate hydroxide with flower-like microstructures. However, as the ratio increases beyond 100, no nanopetals form. The obtained products were spherical aggregates of nanoparticles (Figure 6-4), which was indexed to CeO$_2$ by XRD (Figure 6-5). If the ratio was kept between 20 and 100, a combination of cerium compound microflowers and ceria nanoparticles was obtained.
Figure 6-4. (a)-(b) SEM images of as-prepared ceria; (c) TEM image of as-prepared ceria in (a-b); (d) SAED pattern of as-prepared ceria in (c). The molar ratio of Ce$^{4+}$ to H$_2$O is 1:100.
6.3.3 Formation Mechanism of Nanopetal Cerium Compound

In this hydrothermal condition, two competing reaction processes existed: the hydrolysis of Ce\(^{4+}\) and the redox reaction between Ce\(^{4+}\) and ethanol. Both reactions are preceded by a reversible formation of a complex between Ce\(^{4+}\) and ethanol. This complexation is indicated by the change of color, from a clear yellow red to a deep wine red. The chemical reaction of the oxidation of ethanol by Ce\(^{4+}\) can be formulated as

\[
2\text{Ce}^{4+} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow 2\text{Ce}^{3+} + \text{CH}_3\text{CHO} + 2\text{H}^+ \quad (6-1)
\]
Which comprises two half reactions

\[
Ce^{4+} + e^- \rightarrow Ce^{3+} \quad E^0=1.72V \quad (6-1a)
\]

\[
CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^- \quad E^0=0.197 V \quad (6-1b)
\]

On the basis of \(E^0\), the Gibbs free energy change of reaction (6-1) could be \(-370 kJ/mol\), implying a very strong tendency for reaction (1) to progress toward the right-hand side. The two reactions are favored energetically. It is the kinetic factors that determine which reaction would take place more favorably.

Michael Ardon \(^{13}\) has investigated in detail the kinetics and mechanism of oxidation of ethanol by ceric perchlorate. The overall reaction could be described by the following steps:\(^{13}\)

\[
2Ce^{4+} + EtOH \Leftrightarrow complex \rightarrow 2Ce^{3+} + Me\cdot CHO + 2H^+ \quad (6-2)
\]

The complex undergoes first-order decomposition into Ce\(^{3+}\) and the radical ion. This decomposition was the rate-determining step, followed by quick oxidation of the radical to acetaldehyde by a second Ce\(^{4+}\). Then acetaldehyde could be possibly further oxidized by Ce\(^{4+}\) to acetic acid, which may decompose at elevated temperature to form CO and H\(_2\)O or (CO\(_2\) and H\(_2\)).\(^{14-15}\)

In the hydrothermal system, trivalent Ce\(^{3+}\) (aq) has a strong affinity with OH\(^-\) (aq). The cation will thus combine with OH\(^-\) (aq), forming the Ce(OH)\(^{2+}\) (aq) polyatomic group \(^{16}\). At elevated temperatures, CO\(_3^{2-}\) will bond with the positive-charged groups to yield the solid Ce(OH)CO\(_3\) at high supersaturation. The nascent crystallites act as seeds for succeeding crystal growth. When the concentration of the ceric ion decreased to some extent, the hydrolysis of Ce\(^{4+}\) overwhelmed the reduction of Ce\(^{4+}\), so that a small amount
of ceria was precipitated out. Hence, by changing the metal ion-to-water ratio, the relative rates of hydrolysis of Ce$^{4+}$ and reduction of Ce$^{4+}$ by ethanol could be controlled.

Regarding the growth process, although it is still not clear why the nanopetals self-assemble into the resulting flower-like microstructures, we think in the present study the growth of nanopetals favored by \{0001\} faces is possibly governed by crystal structure, surface energy and driving force. The \{0001\} face is a close-packed face of the lowest surface energy in hexagonal system. It is the general principle in forming a self-assembled nanostructure to maximize the packing density. The two-dimensional nucleation growth is possibly because higher supersaturation at the edges is expected than the central area under hydrothermal condition, and higher topological defect density is expected at the edge, both of which favor radial growth.

### 6.4 Surface Properties of the Different CeO$_2$ Morphologies

Raman spectroscopy was used to characterize the oxygen species formed on nanopetal CeO$_2$ surface. The surface oxygen species were proven by switching 10\% $^{16}$O$_2$ (balance Ar) to 10\% $^{18}$O$_2$ (95\% $^{18}$O$_2$ / 5\% $^{16}$O$_2$, balance Ar). The Raman spectrum in Figure 6-6 shows bands at 831cm$^{-1}$ which is assigned to the adsorption of $\eta^2$ peroxide species.$^{18-19}$ Former studies revealed that CO could interact with species characterized by vibrational bands at 831cm$^{-1}$. In this work, CH$_4$ was used to study the oxidation reactivity of the adsorbed species. The band at 831cm$^{-1}$ disappeared after exposure to CH$_4$ for 20 min(Figure 6-6c) and then re-appeared when exposed to O$_2$ atmosphere again(Figure 6-6d). The result indicated that the absorption and removal of surface species is reversible.
Figure 6-6. Raman spectra of a CeO$_2$ microflower sample collected (after evacuation at 50ºC) at room temperature sequentially in (a) Ar, (b) 10% O$_2$+Ar, (c) 10% CH$_4$+Ar, and (d) 10% O$_2$+Ar.

Figure 6-7 compares the Raman spectrum of the ceria microflowers sintered at 500°C to that of spherical ceria nanoparticles. The ceria samples had been reduced in 5% H$_2$ at 400°C and then were exposed to 10% O$_2$ (balance argon) at room temperature. Both morphologies demonstrate the 831 cm$^{-1}$ peak which has been previously assigned to an adsorbed peroxide species. The 1128 cm$^{-1}$ peak observed from the nanoparticles sample has been attributed to a surface superoxide speices and, unlike the 831 cm$^{-1}$ species, has been shown to be directly involved with CO oxidation. Since the intensity of 1128 cm$^{-1}$ peak is much weaker for the microflower sample than for the nanoparticles,
the microflower ceria with its different morphology probably exhibits different catalytic activities towards CO oxidation.

Figure 6-7. Raman spectra characterizing O₂ adsorption (a) on CeO₂ microflowers with aggregated nanoparticles and (b) on CeO₂ nanoparticles, both of which had been exposed to 5% H₂ at 400°C and then exposed to 10% O₂.

6.5 Conclusion

In summary, we have synthesized a unique cerium compound nanostructure via a controlled hydrothermal process. The nanopetals are of ~10 μm in diameter and ~10 nm in thickness. This nanostructure retains high surface area at high temperature due to the unique structure. Raman results indicated that nanopetal CeO₂ stabilizes O₂.
predominantly as a peroxide species on its surface. The bare site for $\eta^2$ peroxide species are easily formed and destroyed. The CeO$_2$ nanoparticles stabilizes O$_2$ as both peroxide and superoxide species.
6.6 References


CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In this thesis, porous nanostructured electrodes and catalysts with high surface area have been developed by different chemical methods including sol-gel, combustion CVD, hydrothermal process, and template-assisted self-assembly process, to promote electrode kinetics and minimize electrode polarization losses.

Electrodes with unique microstructures have been obtained. (1) Interconnected macroporous spinel LiMn$_2$O$_4$ with particle size of 100 nm has been successfully synthesized using an optimized glycine-nitrate combustion process. (2) Nanostructured tin dioxide thin films with columnar grains were deposited by combustion CVD method. These columnar grains were composed of nanoparticles with the size of less than 20 nm. (3) Multi-scale porous MIEC electrode films were prepared using self-assembled polymer foam as the template. These electrodes presented regular macroporous morphology and random mesopores in the walls of the macropores. The primary particle size was about 100 nm. This morphology is ideally suited for electrode applications, because macropores promote rapid gas transport and nanopores provide high surface areas for gas adsorption/desorption and for catalytically active sites for electrode reactions. (4) A modified sol-gel process was used to fabricate porous cathode on honeycomb electrolyte. This process could produce particle size of 10 nm and stronger adhesion between electrode and electrolyte. (5) A novel nanopellet ceria was produced by hydrothermal process. It presented high surface area and was resistant to sinter at high temperature due to its unique structure.

Qualitative correlations of the microscopic features with electrochemical properties of produced materials were studied. For lithium batteries, porous nanostructure
with high surface area promotes the mass transfer and suppresses or relaxes the stress caused by the volume change during lithium insertion and deinsertion. The decreased tortuosity and high surface area improves the rate capability. Macroporous nano-LiMn$_2$O$_4$ particles exhibited better capacity retention and rate capability than those with larger particle size prepared by solid state reaction. The LiMn$_2$O$_4$ powders displayed reversible capacity of about 112 mAh/g at a discharge rate of 49.0 $\mu$A/cm$^2$ (C/5 rate). At a high discharge rate of 2.44 mA/cm$^2$ (10 C rate), the obtainable reversible capacity was 57 mAhg$^{-1}$.

Columnar tin dioxide thin film composed of nanoparticles with the size of 20 nm was found with high capacity, good capacity retention and rate capability due to its unique structure with longitudinal and radial connectivity of active materials. It is about 93% after 80 cycles at a charge/discharge rate of 0.3 mA/cm$^2$. When discharged at 0.9 mA/cm$^2$, the capacity retention obtained was about 64% of the capacity at 0.3 mA/cm$^2$.

For solid oxide fuel cells, the situation is more complicated. This is mainly due to the fact i) that electrode process and morphology are closely related, ii) that the fundamental mechanisms of oxygen reactions on the cathode are not fully understood at the present time, and iii) that the microstructures have complicated and interacted effects on the activation polarization, concentration polarization and sheet resistance. In this research, the results showed that microstructures with high porosity, small particle size and large surface area exhibited low interfacial polarization resistances at intermediate temperatures. And the electroding process was also crucial to produce strong bonding between electrode and electrolyte and reduce the interfacial polarization resistance.

For multiscale porous MIEC electrode films, the interfacial polarization resistances were 0.94 and 0.39 $\Omega$cm$^2$ at 700 and 750°C, respectively, as determined using impedance spectroscopy. The low interfacial resistance is attributed to the promoted mass transport and the enlarged TPBs that are resulted from highly porous and ordered microstructure.
For electrodes consisting of LSM and GDC developed with a modified sol gel process, it showed much lower interfacial polarization resistances than those prepared by slurry coating or spray deposition. The interfacial polarization resistances were 0.65 and 0.16 Ωcm² at 650 and 750°C, respectively. The low interfacial polarization resistances are partly resulted from the enlarged TPBs and the strong bonding between electrode and electrolyte. Moreover, when the particle size was as small as 10 nm, the semi-infinite boundary condition was not satisfied any longer. Hence the mesoscopic overlapping of the space charge and the quantum confinement would have important effects on the ionic and electronic conductivity respectively.

Two main factors would be considered to be beneficial to reduce interfacial polarization resistance with regard to particle size. One is TPB effect. The other is nanosize effects. In view of extrinsic-intrinsic transition of the pure materials, there exist the critical particle size separating the regime of semi-infinite space charge effect and the mesoscopic regime of overlapping space charge effect. TPBs have an important effect on the electrode kinetics. Considering the solid state diffusion, the reaction zone of TPB is actually not a line and should extend over a finite region of surface. When the MIEC particle size satisfies the semi-infinite boundary condition, The TPBs can be increased by increasing porosity and decreasing MIEC particle size, i.e. increasing surface-volume ratio. Nanosize effects would take place when the MIEC particle size is so small that the semi-infinite boundary condition and the charge-neutrality in the bulk of the particle are no longer invalid. The mesoscopic overlapping of the space-charge effects would greatly influence the ionic conductivity and surface catalytic properties.
7.2 Recommendation

Beyond this work, there are still many crucial issues that needed to be clarified in order to quantitatively correlate the microscopic features and their electrochemical properties. As discussed in Chapter 5, when the particle size is so small or film is so thin that the semi-infinite boundary condition is not satisfied any longer. Hence the nanosize effects including mesoscopic overlapping of the space charge or depletion layer took place. In the view of extrinsic-intrinsic transition of the pure materials, two main factors would be considered for reducing interfacial polarization resistance. One is TPB effect. The other is nanosize effects. When the particle size satisfies the semi-infinite boundary condition, TPBs have an important effect on the electrode kinetics. The TPBs can be increased by increasing porosity and decreasing particle size, i.e. increasing surface-volume ratio. The overlapping of the space-charge would greatly influence the ionic conductivity, electronic conductivity and surface catalytic properties. However, the conclusive proof of this effect is still lacking. Assuming a strong bonding between electrode and electrolyte, to explore the line where the electrode kinetics is mainly determined by triple phase boundary effect or nanosize effects would be of great technical value for the insights it allows, and of paramount physical and electrochemical importance.

At present, it is still difficult to quantitative analyze microstructure prepared by bottom-up techniques. Hence, development of layered heterostructures by top-down techniques is a better choice to fabricate highly defined geometry, periodicity, interfacial spacing and layer sequence for quantitatively analysis of correlation between electrochemical properties and microscopic features. Beyond critical layer space distance, the properties could be considered to be determined mainly by TPBs. To some point, it may elucidate the correlation between TPB length (when the layer spacing width is much wider than the effective TPB width) and the resulted polarization resistance, the transition layer spacing (i.e. effective TPB width) when overlapping space-charge effects take
place. Because the length scales that determine the nanosize effects are different for ionic and electronic conductors, we would expect two different critical sizes that would be determined at different temperatures from 1112 heterolayers or IE hyterolayers, in which E represents electronic conductors, including metallic conductors and semiconducting oxides and I represents ionic conductors. Oxygen ionic conductors, such as Y-doped CeO2, Y-doped Bi2O3 or Y-doped ZrO2, are candidates for investigation. The thickness of the both films changes but the cross area of each kind of film is kept unchanged. Conductivity is measured along parallel films as the parameters of the thickness temperatures and oxygen concentration in air.

As to the IE hyterojunction, if a p-type (La,Sr)MnO3 semiconductor layer is used, only the semiconductor layer changes the thickness and the ac-impedance technique is used to monitor the interfacial phenomena by analyzing RC combination circuits as the variance of the thickness temperature, and oxygen concentration.
APPENDIX A

PUBLICATION AND PATENTS

Publications:


[10] Zhen Zhou, Siwen Li, Yuelan Zhang and Meilin Liu, “1H-1,2,3-Triazole based polymer materials for proton exchange membranes”, PMSE Preprints, 2006, 94, 609.


[5] Siwen Li, Zhen Zhou, Yuelan Zhang and Meilin Liu, 1H-1, 2, 4-Triazole: an Ideal Proton-Conducting Solvent for Proton Electrolytes, Chemistry of Materials, 2005, 17 5884.


Patent:

Siwen Li, Zhen Zhou, Yuelan Zhang, Meilin Liu and Wen Li “Sulfoyl-grafted heterocycles based materials for Proton-Conducting Electrolytes”, 2005, provisional patent filed.

Presentations:


[2] Zhen Zhou, Siwen Li, Yuelan Zhang and Meilin Liu, 1H-1,2,3-Triazole based polymer materials for proton exchange membranes, *231st ACS National Meeting*, March 26-30, 2006, Atlanta, GA.


