

# CORROSION-RESISTANT COATING FOR CARBONATE FUEL CELL COMPONENTS

*Prepared For:*

**California Energy Commission**  
Energy Innovations Small Grant Program

*Prepared By:*

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**FEASIBILITY ANALYSIS AND FINAL EISG REPORT**

May 2005  
CEC-500-2005-081



# **ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM**

## **FEASIBILITY ANALYSIS REPORT (FAR)**

### **CORROSION RESISTANT COATING FOR CARBONATE FUEL CELL COMPONENTS**

#### **EISG AWARDEE**

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Grant #: 00-05

Grant Funding: \$75,000

Term: October 15, 2000-April 15, 2002

PIER Subject Area: Environmentally Preferred Advanced Generation

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## PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to \$62 million of which \$2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University, which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to \$75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
  - Appendix A: Final Report (under separate cover)
  - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at:

<http://www.energy.ca.gov/research/innovations>

or contact the EISG Program Administrator at (619) 594-1049 or email [eisgp@energy.state.ca.us](mailto:eisgp@energy.state.ca.us).

For more information on the overall PIER Program, please visit the Commission's Web site at <http://www.energy.ca.gov/research/index.html>.

# Corrosion Resistant Coating for Carbonate Fuel Cell Components

## EISG Grant # 00-05

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Grant Funding:	\$75,000
Grant Term:	October 15, 2000 – April 15, 2002

### Introduction

Molten carbonate fuel cells are energy-efficient and environmentally clean devices for the generation of electric power. They can be fueled directly with natural gas or biomass-derived gasses. High capital cost and durability problems have slowed deployment of these fuel cells. The durability problems derive primarily from corrosion of system components by the carbonate. Although molten carbonate fuel cells (MCFC) are now being offered in sizes from 0.3 MW to 3.0 MW, warranties are limited, and service contracts are expensive (~\$200/kW per year).

Molten carbonate fuel cells offer higher potential energy efficiency (~60%) than phosphoric acid fuel cells (~45%), micro-turbines (~28%), mid-sized gas turbines (~38%), or natural-gas-fueled reciprocating engines (~38 %). A molten carbonate fuel cell would be an excellent candidate for grid-connected distributed generation if its cost and durability problems were resolved. In a distributed-generation scenario the molten carbonate fuel cell could cleanly, quietly, and efficiently provide electricity. Molten carbonate fuel cells could be sited in dense urban areas without a negative effect on air quality.

In a recent (2003) survey conducted by the California Power Authority, molten carbonate fuel cells provided the lowest cost electricity (\$0.13/kWh before incentives) of any fuel cell available for installation. Maintenance was included in the cost estimates.

In this project the researcher proposed applying a sol-gel coating to reduce the corrosion of the cathode current collector (CCC) and the cathode material. Experts consider corrosion in these areas the most important factor impairing the useful life of carbonate fuel cells. The researcher proposed depositing a  $\text{LiCoO}_2$  coating on a porous nickel cathode substrate and a corrugated CCC and testing the performance of these components with the new coating. The researcher chose  $\text{LiCoO}_2$  for the coating material because it has high electronic conductivity and high corrosion resistance.

### Objectives

The goal of this project was to determine the feasibility of using a sol-gel coating ( $\text{LiCoO}_2$ ) to reduce the corrosion of cathode current collector and NiO cathode in molten carbonate fuel cells. The researcher established the following project objectives:

1. Improve the corrosion resistance of the NiO cathode and cathode current collector.
2. Increase the lifetime of molten carbonate fuel cells by 100%.
3. Determine economic feasibility of the coating.
4. Determine technical feasibility by evaluation of  $\text{LiCoO}_2$  film in the fuel cell operating environment.

## Outcomes

1. Data collected in this project indicated a decay rate of about 10mV/1000 h. This rate was approximately the same for coated and uncoated samples. Electrolyte creepage loss was one-third less on the coated CCC than on the non-coated control sample. Electrical resistance of the coated CCC was stable for an 1800-hour test.
2. The researcher claimed MCFC life could be extended by a factor of two to five but did not include a product-life-cycle analysis in the final report to support that claim. Some data in the final report indicate that fuel-cell life could be extended with the LiCoO<sub>2</sub> sol-gel coating. On the other hand, one test apparently failed at 3700 hours. No explanation was given for the early termination of that test.
3. The researcher did not provide economic feasibility information. He stated this sol-gel process is inexpensive (<\$1 per square meter).
4. The researcher developed coating methods for both the porous nickel and corrugated CCC. The coatings were successfully applied.

## Conclusions

1. Data presented in the final report support the claim of reduced corrosion of the CCC when coated with LiCoO<sub>2</sub>.
2. No product-life-cycle analysis was included in the final report. The performance charts in that report indicate fuel-cell failure in as little as 3700 hours. Scientific literature contains data for single-cell, fuel-cell tests surpassing 15,000 hours with decay rates of less than 5mV/1000 hours. The researcher may not have adequately characterized the life-extension benefits of the LiCoO<sub>2</sub> coating.
3. The PA cannot determine economic feasibility of the coating process without knowing the life extension of the MCFC and the coating cost relative to the costs of other components.
4. The researcher was able to apply the sol-gel coating to the critical MCFC components. The coating did not degrade the performance of the components.
5. The researcher should be encouraged to continue this line of work. It appears that substantial progress has been made toward reducing corrosion in the molten carbonate fuel cell. Unfortunately the researcher did not present project data in the final report in a manner that clearly proves the feasibility of this project.

## Benefits to California

Molten carbonate fuel cells offer the potential of high fuel efficiency and extremely low exhaust emissions. These properties are highly desirable for grid-connected, distributed-power systems. Successful introduction of a durable MCFC at a reasonable capital cost could speed the introduction of distributed generators into the power grid. Overall fuel efficiency would be greatly improved for generation of electricity in California, and air emissions would be greatly reduced. Insufficient data were presented to quantify the benefits.

## Recommendations

The researcher has made significant progress in addressing the durability of MCFCs. Unfortunately the data presented in the final report (Appendix A) is not in a form that allows one to determine the magnitude of the advance. The PA recommends the following:

1. Clearly address the project objectives in a technical report. Explain the rapid decline in performance and the early cell failure shown in Figure 10a of Appendix A.

2. Quantify the results and compare to existing life and durability data for near-commercial MCFCs.
3. Work with a major developer of MCFCs such as FuelCell Energy to determine the value of the coating in a real-world product.
4. Obtain patent protection for the process used to coat the MCFC components.
5. Analyze material safety data for the  $\text{LiCoO}_2$  to ensure compliance with existing regulation.

## Stages and Gates Methodology

The California Energy Commission utilizes a stages and gates methodology for assessing a project's level of development and for making project management decisions. For research and development projects to be successful they need to address several key activities in a coordinated fashion as they progress through the various stages of development. The activities of the stages and gates process are typically tailored to fit a specific industry and in the case of PIER the activities were tailored to be appropriate for a publicly funded energy research and development program. In total there are seven types of activities that are tracked across eight stages of development as represented in the matrix below.

**Development Stage/Activity Matrix**

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
Activity 1								
Activity 2								
Activity 3								
Activity 4								
Activity 5								
Activity 6								
Activity 7								

A description the PIER Stages and Gates approach may be found under "Active Award Document Resources" at: <http://www.energy.ca.gov/research/innovations> and are summarized here.

As the matrix implies, as a project progresses through the stages of development, the work activities associated with each stage needs to be advanced in a coordinated fashion. The EISG program primarily targets projects that seek to complete Stage 3 activities with the highest priority given to establishing technical feasibility. Shaded cells in the matrix above require no activity, assuming prior stage activity has been completed. The development stages and development activities are identified below.

<b>Development Stages:</b>	<b>Development Activities:</b>
Stage 1: Idea Generation & Work Statement Development	Activity 1: Marketing / Connection to Market
Stage 2: Technical and Market Analysis	Activity 2: Engineering / Technical
Stage 3: Research & Bench Scale Testing	Activity 3: Legal / Contractual
Stage 4: Technology Development and Field Experiments	Activity 4: Environmental, Safety, and Other Risk Assessments / Quality Plans
Stage 5: Product Development and Field Testing	Activity 5: Strategic Planning / PIER Fit - Critical Path Analysis
Stage 6: Demonstration and Full-Scale Testing	Activity 6: Production Readiness / Commercialization
Stage 7: Market Transformation	Activity 7: Public Benefits / Cost
Stage 8: Commercialization	

## Independent Assessment

For the research under evaluation, the Program Administrator assessed the level of development for each activity tracked by the Stages and Gates methodology. This assessment is summarized in the Development Assessment Matrix below. Shaded bars are used to represent the assessed level of development for each activity as related to the development stages. Our assessment is based entirely on the information provided in the course of this project, and the final report. Hence it is only accurate to the extent that all current and past work related to the development activities are reported.

**Development Assessment Matrix**

Stages Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technology Develop- ment	5 Product Develop- ment	6 Demon- stration	7 Market Transfor- mation	8 Commer- cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

The Program Administrator’s assessment was based on the following supporting details:

### Marketing/Connection to the Market

The researcher has not indicated a path to market for the coating investigated in this project. One possibility would be a business arrangement with a developer of MCFCs. Teaming with a developer of MCFC could provide valuable input to the researcher during the next phase of coating development.

### Engineering/Technical

This project advanced the science and technology of coating MCFC components with a LiCoO<sub>2</sub> material. The researcher should work with a manufacturer of MCFC products to assess the potential life extension of coated components in the manufacturer’s products. This will establish a true baseline for product component life with and without the coatings.

### Legal/Contractual

The researcher did not report on intellectual property protection. No legal or contractual problems were revealed.

## **Environmental, Safety, Risk Assessments/ Quality Plans**

Quality Plans include Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety and Environmental. None of these plans had been started at the time of the final report.

## **Strategic**

This product has no known critical dependencies on other projects under development by PIER or elsewhere

## **Production Readiness/Commercialization**

The researcher has completed the first of many laboratory tests and is not yet ready for commercialization. Working with a MCFC developer at this time could speed the introduction of this technology into the marketplace.

## **Public Benefits**

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California.

The primary benefit to the ratepayer from this research is the increased affordability of electricity in California. If the proposed coating extends the life of a MCFC by 100%, the effective cost of electricity generated by a MCFC would be significantly reduced. The longer life would also reduce maintenance costs and downtime. Since the MCFC can be up to 60% efficient, the cost of the electricity produced could be considerably lower than from other distributed-generation technologies with efficiencies in the 25% to 38% range. First cost and maintenance costs also affect the cost of the electricity.

## **Program Administrator Assessment**

After taking into consideration: (a) research findings in the grant project, (b) overall development status as determined by stages and gates, and (c) relevance of the technology to California and the PIER program, the Program Administrator has determined that the proposed technology should be considered for follow-on funding within the PIER program.

Receiving follow-on funding ultimately depends upon: (a) availability of funds, (b) submission of a proposal in response to an invitation or solicitation, and (c) successful evaluation of the proposal.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

**ENERGY INNOVATIONS SMALL GRANT  
(EISG) PROGRAM**

**EISG FINAL REPORT**

**CORROSION RESISTANT COATING FOR CARBONATE FUEL  
CELL COMPONENTS**

**EISG AWARDEE**

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Grant #: 00-05

Grant Funding: \$75,000

Term: October 15, 2000-April 15, 2002

PIER Subject Area: Environmentally Preferred Advanced Generation

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- Renewable Energy
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

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<http://www.energy.ca.gov/research/innovations>

For more information on the overall PIER Program, please visit the Commission's Web site at:  
<http://www.energy.ca.gov/research/pier>

Inquires related to this final report should be directed to the Awardee ( see contact information on cover page) or the EISG Program Administrator at (619) 594-1049.

## Executive Summary

The primary objective of this research is to solve one of the most serious problems in molten carbonate fuel cells; corrosion of cathode current collector and lithiated NiO cathode, which has been a major lifetime-limiting factor. The specific objectives of the program are:

- Development of cost-effective, environmental benign sol-gel coating solution for LiCoO<sub>2</sub> material.
- Development of sol-gel coating technique for deposition of LiCoO<sub>2</sub> film on 316L CC and porous Ni cathode.
- Characterization of LiCoO<sub>2</sub> films.
- Evaluation of LiCoO<sub>2</sub> film in fuel cell operating environment.

All the objectives have been successfully accomplished. The proof of feasibility of :1) preparation of stable LiCoO<sub>2</sub> sols, 2) coating thin dense films of the sols on the CCC and cathode substrate, have been firmly established. Furthermore

The efforts recommended include: 1). Further development of corrosion resistant coating by optimization of composition and process parameters; 2) Further development and scaling up of coating solution and coating technology; 3) Study/testing the coatings in single fuel cell and optimize the performance of the coatings.

After successful completion of next phase work, the process will be ready for use in commercial stacks.

## **Abstract**

The proposed research aims to solve the corrosion problem of cathode current collector and lithiated NiO cathode. In this research effort, a sol-gel coating process was developed to improve the performance of cathodes and cathode current collector. By carefully selecting the coating materials, the corrosion resistance was enhanced dramatically. Consequently, the lifetime and power generation efficiency of fuel cell was improved simultaneously.

## Table of Contents

Preface	
Executive Summary	
Abstract	
I. Introduction.....	2
1.1. Technical Background.....	4
1.1.1. Sol-gel Coating Technique .....	4
1.1.2 Sol-gel process .....	5
1.2. Project Objectives .....	6
II. Project Approach.....	6
III. Project Outcomes .....	7
3.1 Preparation of coating solution .....	7
3.2 Coating Technique .....	7
3.2.1 Coating on stainless steel substrate .....	7
3.2.2 Coating on porous Ni cathode.....	7
3.3. Characterization of the Coating .....	7
3.3.1. Phase composition analysis.....	8
3.3.2. Microstructure Characterizations .....	8
A. LiCoO <sub>2</sub> coating on stainless steel cathode current collector (CCC) .....	8
B. LiCoO <sub>2</sub> coating on nickel plate .....	9
3.4 Evaluation of Resistance of cathode/CCC contact.....	10
3.4.1. Out-of-cell Test .....	11
3.4.2. Single Cell Test .....	12
IV. Conclusions and Recommendations .....	12
V. Feasibility Analysis.....	13
Appendix: I. References.....	14
Appendix II. Proprietary Information .....	15

## I. Introduction

The carbonate fuel cell offers a highly efficient and environmentally benign method for electric power generation. It is also an ideal system to be used with reformed natural gas and gasified coal. However, corruptions of system components in the carbonate corrosive environment, such as electrolyte loss, reduction of catalyst life, and corrosion of other stack components, are still serious longevity problems in fuel cells.<sup>i</sup> This proposal will target at reducing the corrosion of cathode current collector (CCC) and cathode material, which are considered two most important factors for extending carbonate fuel cell useful life.

Fig. 1 shows the structure of a single cell package. CCC is directly contacted with the cathode, which is soaked with molten carbonates electrolyte. Currently, the CCC is made of 316L stainless steel, due to its low resistance and price. Hot corrosion of CCC involves the formation of a  $\text{LiFeO}_2$  outer and Cr-rich inner surface oxide layer, which is somewhat protective but electrically insulating. Based on FuelCell Energy's (FCE, former Energy Research Corporation) analysis, over 50% electrolyte loss comes from CCC hot corrosion and electrolyte creepage on CCC surface. Significant electrolyte loss can cause electrode performance decay, matrix ionic resistance increase, and reactant cross-over increase. The interfacial resistance between the cathode and CCC due to the hot corrosion of CCC ( $\sim 300\Omega\text{-cm}$  resistivity for  $\text{LiFeO}_2$  as opposed to  $\leq 0.1\Omega\text{-cm}$  for lithiated NiO) will also cause significant ohmic voltage loss in the cell. At the beginning of life, the interfacial resistance is about  $60\text{m}\Omega\text{-cm}^2$ , which is equivalent to  $\sim 5\%$  power loss. As the oxide thickens with time, the interfacial resistance continues to increase. It was estimated that about 0.1 mil thick of  $\text{LiFeO}_2$  can cause more than 50 mV ohmic voltage loss at  $160\text{mA}/\text{cm}^2$ .

Cost-effective materials that can reduce corrosion while forming conductive oxides are highly desired. Therefore, an opportunity exists to develop a new current collector material or a unique coating to: 1) reduce initial resistance and resistance increase with time, 2) reduce material corrosion, and 3) reduce electrolyte loss. If these issues are successfully addressed, the carbonate fuel cell useful life can be increased at least by a factor of two.

NiO cathode material is transformed into lithiated nickel oxide by its interaction with the electrolyte (lithium and potassium carbonate). The further corrosion of lithiated NiO cathode involves the dissolution of NiO into the carbonate electrolyte, transport of the soluble species into the electrolyte matrix, and precipitation of Ni metallic particles within the electrolyte structure.<sup>ii,iii</sup> When significant amount of the Ni metallic precipitates is accumulated in the electrolyte matrix, an internal short circuit can occur, and thus net power output is reduced.

Currently, there are indications that the use of  $\text{LiNaCO}_3$  electrolyte has reduced the dissolution of the cathode to acceptable levels. However, compared to  $\text{LiKCO}_3$  electrolyte,  $\text{LiNaCO}_3$  has: 1) lower ionic conductivity, 2) lower electrochemical activity, 3) higher metallic corrosion. Therefore,  $\text{LiKCO}_3$  electrolyte has higher efficiency than

LiNaCO<sub>3</sub>. It would be more efficient to use LiKCO<sub>3</sub> as electrolyte, meanwhile reduce cathode dissolution rate.

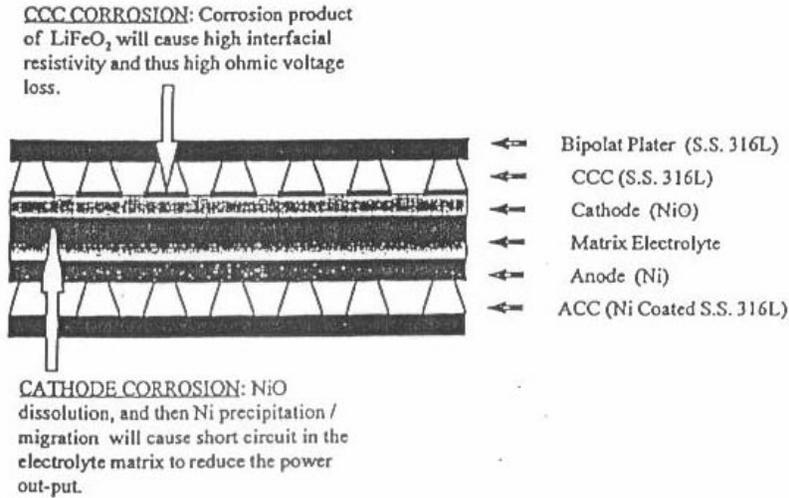


Fig.1 Schematic illustration of single-cell package. (NiO cathode and 316L CCC corrosion location are shown)

Current attempts are being made to find spinels and perovskites, as substitutes for the lithiated nickel oxide cathodes, which are expected to be less corrodible in the electrolyte. Among these, LiCoO<sub>2</sub> is the most attractive because of its low solubility (or no metallic deposit formation) and relatively low resistivity (1~3 Ω.cm) in carbonate environment. The application of this LiCoO<sub>2</sub> can either be in the form of bulk material or as a protective coating. However, if the cathode were made entirely from LiCoO<sub>2</sub>, the cost would be too high. Therefore, using it as a coating material seems to be a cost-effective approach for improving the performance of cathode. The material is also ideal to be used as a corrosion-resistant coating on CCC to reduce the electrolyte loss and contact resistance between cathode and CCC. Therefore, the primary focus of this project is to deposit a LiCoO<sub>2</sub> coating on porous Ni cathode and CCC, and test their performance, including electronic resistance and corrosion resistance, in an out-of-cell fashion.

## 1.1. Technical Background

### 1.1.1. Sol-gel Coating Technique

Coating thin film on large scale (9000 cm<sup>2</sup> area for current commercial design) carbonate fuel cell components has prevented the utilization of conventional coating methods. The most common technique used for thin film coatings include chemical vapor deposition (CVD), plasma activated vapor deposition, sputtering (PVD), electron-beam deposition. Most of these techniques require vacuum coating chambers. To coat such a large size component, a large capital investment is required for the equipment. In addition, these techniques are not suitable for coating the porous Ni substrate and corrugated CCC. In this case, sol-gel method appears to be an ideal alternative. Sol-gel is a total solution method. The coating solution can readily enter the porosity and fully cover the particles that constitute the porous substrate. After certain drying and heat treatment, an oxide film will be formed, while the porosity will be maintained in cathodes. If the porosity of the porous substrate is very fine, the coating process can be accomplished with the assistance of vacuum system, which can remove the gas and bring the solution into the porosity. Sol-gel method is also perfectly viable for coating complex shaped CCC.

One concern associated with this particular application is the integrity of coating on NiO cathode due to a substrate volume expansion from Nickel oxidation. Most MCFC developers are fabricating cathodes from nickel powders, which will be oxidized and lithiated in-situ when the MCFC is first heated to operating temperature. Nickel oxidation is accompanied by a volume expansion. When a sol-gel precursor coating applied on Ni powders, during the heat-treatment, two possibilities exist:

- 1) Ni powders will not be oxidized: Ni powders are covered by a dense sol-gel precursor coating layer, the chance of O<sub>2</sub> diffusion to the substrate surface is slim. Meanwhile, O<sub>2</sub> will be consumed in the formation of LiCoO<sub>2</sub> before it reaches Ni surface to oxidize Ni. Therefore, Ni powders are fully protected.
- 2) Ni powders will be oxidized: Oxygen can diffuse to the surface of Ni powders. Oxidation and volume expansion is expected. Cracks will be induced in the LiCoO<sub>2</sub> coating. Therefore, the dissolution of Ni cannot be completely prevented, however, this dissolution can still be greatly reduced depending on the coating coverage. Fuelcell life still can be prolonged in this way.

As for CCC coating, oxidation and volume expansion is not a concern. LiCoO<sub>2</sub> coating should provide excellent protection for CCC.

Coating thickness can easily be controlled by the viscosity of the solution. Cathodes from nickel powders having a particle size less than 5 microns diameter for the purpose of obtaining cathodes that, after oxidation, have a substantial amount of submicron porosity. Before oxidation the porosity is 75%, after oxidation, the porosity is around 65%. With one thin layer coating (0.1-0.5 micron), the porosity change should be around 1%, therefore, the performance of cathode should not be affected. While for CCC coating, thicker coating (>2 micron) should provide better corrosion protection.

### 1.1.2 Sol-gel process

Sol-gel method will be used to coat  $\text{LiCoO}_2$  film on porous Ni cathode, to improve its performance as a cathode in molten carbonate fuel cell. Sol-gel is a cost-effective deposition method, which is capable of uniformly coating thin film on large-scale complex-shaped component. Additional advantages of this method include:<sup>iv,v</sup>

- Environmentally friendly: use all aqueous solution.
- Low capital cost: requiring only simple equipment.
- Tailorable microstructure: coating could be dense or porous.
- Controllable stoichiometric compositions: able to coat multi-component film.
- High degree of uniformity over large area.
- Capable of continuous coating process.
- Capable of application on conductive and nonconductive substrates.

A schematic illustration of a typical sol-gel process is given in Fig. 2. The most traditionally used starting materials for sol-gel thin film process are metal alkoxides  $\text{M}(\text{OR})_x$  where R stands for an alkyl group. Normally, the alkoxide is dissolved in alcohol and then hydrolyzed by the addition of water under acidic, neutral or basic conditions to form a sol, a stable aqueous colloidal dispersion containing primary particles or aggregates of primary particles. Sols can be mixed or doped with metal salts solutions, such as nitrates or acetates, to form precursors for multi-component oxides. When the water or alcohol is removed from the sols, a rigid gel will form and the sol-gel process is completed. Sols can be applied onto the substrates to form a sol-gel film by spinning, spraying, electrophoretic or dipping method. Among these, dipping and electrophoresis are capable of applying coating onto complex shaped components. Scale-up of both techniques is just a matter of building bigger tanks, and thus easily implementable at very low capital cost.

One concern with the traditional sol-gel process is the raw material cost. However, it will become a major problem only in the case of fabricating bulk materials. It should not be an issue for the thin film coating application. It is estimated that a  $1\mu\text{m}$  thickness sol-gel coating of  $\text{Al}_2\text{O}_3$  on aluminum alloy is only about  $\$0.29/\text{m}^2$ ,<sup>vi</sup> which is quite acceptable for carbonate fuel cell commercial application. Another concern about this process is the thickness of the coating. Normally it is easy to obtain the film thickness in the range of  $0.1\text{-}0.5\mu\text{m}$  by controlling the solution viscosity. For film thickness  $\geq 2\mu\text{m}$ , multi-coating is an approach to increase the thickness. An alternative approach is to use a modified sol-gel method, in which acetates are used as precursor material, while ethyl alcohol as solvent. By using this method, C.T.Lin<sup>vii</sup> has successfully prepared lanthanum strontium manganate ( $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ) film with a thickness of  $2\mu\text{m}$ . A further advantage of this method is the low cost of the precursor materials. Acetates are very common, commercial available chemical products.

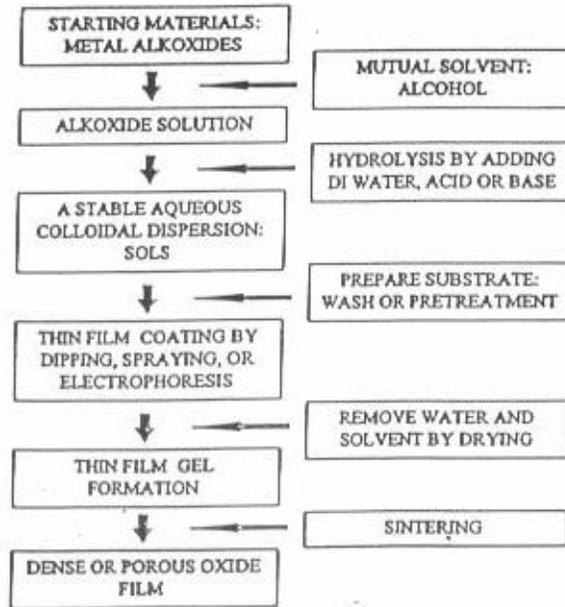


Fig. 2 Schematic illustration of sol-gel process for thin film coatings: this low-cost process is ideally suited for large complex-shaped fuel cell components.

## 1.2. Project Objectives

The objectives in this proposed research are:

- Development of cost-effective, environmental benign sol-gel coating solution for  $\text{LiCoO}_2$  material.
- Development of sol-gel coating technique for deposition of  $\text{LiCoO}_2$  film on 316L CCC and porous Ni cathode.
- Characterization of  $\text{LiCoO}_2$  films.

Evaluation of  $\text{LiCoO}_2$  film in fuel cell operating environment.

## II. Project Approach

To improve the corrosion-resistant capability of CCC and cathode, and consequent its performance in molten carbonate fuel cell,  $\text{LiCoO}_2$  coating will be deposited onto the corrugated CCC and porous Ni cathode by sol-gel method. The coating material possesses the properties of high electronic conductivity, high corrosion-resistance, and good catalytic effects. It is expected that the corrosion of the cathode will be greatly reduced by applying this coating, while the porous structure of Ni cathode remains. The coating will be carried out on small coupons. Out-of-cell characterizations will be performed on these coupons to determine thin film properties. After the feasibility demonstration, application of this technique to carbonate fuel cell components will be further pursued by seeking cooperation with fuel cell company, such as FuelCell Energy.

### **III. Project Outcomes**

#### **3.1 Preparation of coating solution**

The variety of sol-gel coating solutions were prepared and tested, including routes of metal alkoxide, inorganic salts. Several formulations were identified. The resultant sol-gel solution is very stable at room temperature without precipitation in 4 weeks.

#### **3.2 Coating Technique**

##### **3.2.1 Coating on stainless steel substrate**

The coating solution was first applied onto steel substrates by using dip coating technique. The coating was uniform on flat surface steel. However, for those cathode current collectors that were made of steel sheet that indented into grooves, excess solution will stay in the grooves because of capillary force and result in powder during sintering instead of an uniform coating. Therefore, a spin-off process was developed in combination with dip-coating. After dipping in solution tank, the coated substrates were spun by using a specially designed holding apparatus to remove excess solvent. The coating samples were then dried in oven at 200 °C and then fired in furnace at 350°C, 450°C, 550°C and 650°C respectively. The resultant powder was ground and sent to Camet Research Inc for X-ray diffraction analysis.

##### **3.2.2 Coating on porous Ni cathode**

Porous Ni cathode sheet coating was processed in a slightly different way. It was immersed in the above coating solution. To assist the removal of the air held in porosity, vacuum was applied. Coating thickness was controlled by varying the duration of the immersion and the viscosity of the solution. After coating, the samples was dried in a furnace at 110 °C to form a gel film, and further heat-treatment at temperatures up to 650°C in air resulted in a dense oxide coating.

#### **3.3. Characterization of the Coating**

Microstructure of the thin film is very important for corrosion protection and component performance. Dense, thick coating is required for CCC for better corrosion resistance, while thin coating may be necessary for cathode to maintain performance. For dense film finish, however, cracking may result from the thermal expansion mismatch between the film and substrate. Therefore, the film microstructure was optimized for different purposes. The film microstructure was

tailored through adjusting solution parameters, coating conditions, drying environment, and firing temperature.

### 3.3.1. Phase composition analysis

Sol-gel based  $\text{LiCoO}_2$  coating was characterized first by using X-ray diffraction analysis. Following figures show the spectrum for the coating exposed to different temperature from  $350^\circ\text{C}$  to  $650^\circ\text{C}$ . The  $\text{LiCoO}_2$  phase started to form at  $450^\circ\text{C}$ .

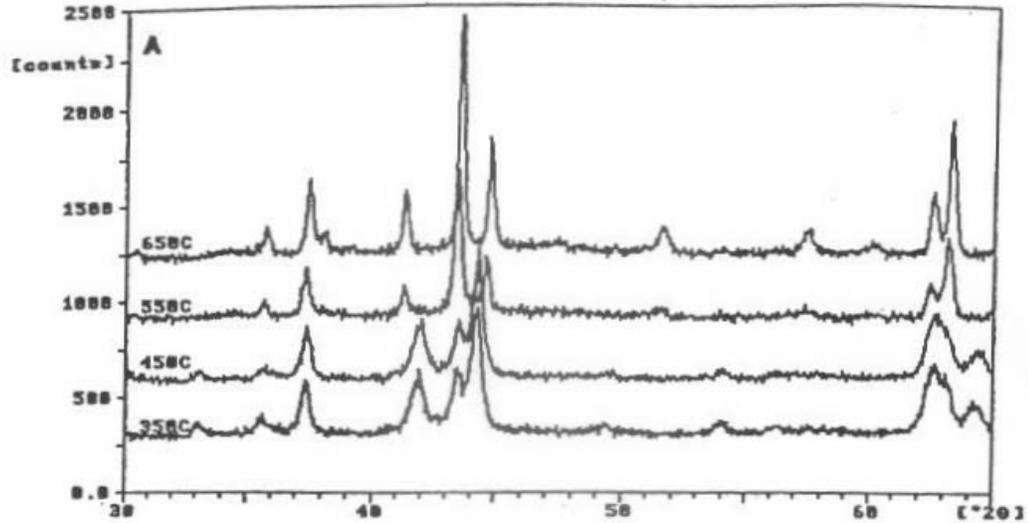


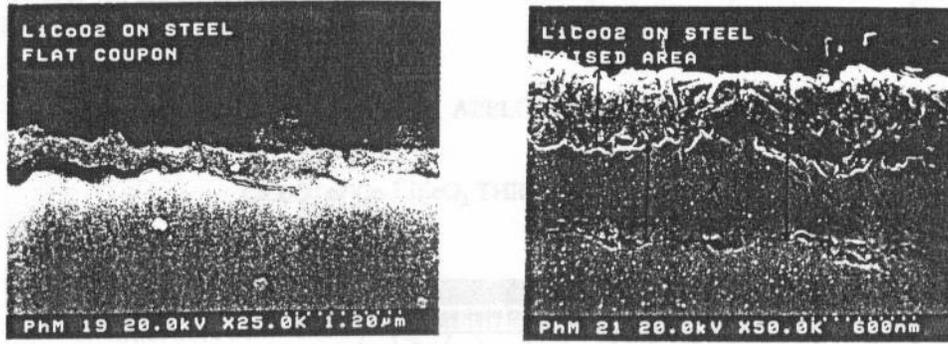
Fig.3 X-ray diffraction spectrum for  $\text{LiCoO}_2$  Sols synthesized at different temperatures.

### 3.3.2. Microstructure Characterizations

#### A. $\text{LiCoO}_2$ coating on stainless steel cathode current collector (CCC)

Sol-gel based  $\text{LiCoO}_2$  coating on CCC was characterized by using Scanning Electronic Microscopy (SEM). The densification of coating samples was conducted at  $650^\circ\text{C}$  in air. The SEM photos show the dense, uniform  $\text{LiCoO}_2$  coating.

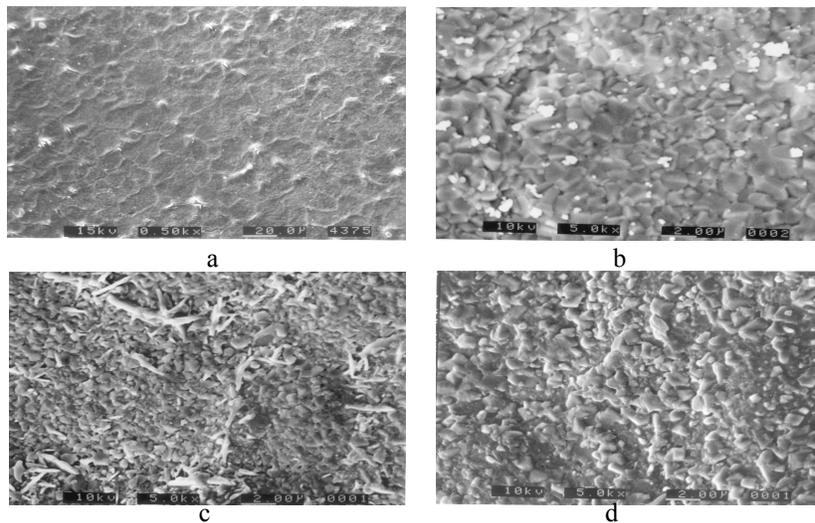
Figure 4 shows the cross section of the coatings on flat and perforated CCC. Fig. 5 shows the coating surface morphology of samples annealed at  $350^\circ\text{C}$  to  $650^\circ\text{C}$ . The coatings are very dense.



a

b

Fig.4. a) LiCoO<sub>2</sub> coating on flat CCC, b) LiCoO<sub>2</sub> coating on perforated CCC



a

b

c

d

Fig. 5. Coating surface morphology for which is annealed at a)350°C, b) 450°C, c) 550°C and d) 650°C.

## B. LiCoO<sub>2</sub> coating on nickel plate

LiCoO<sub>2</sub> coating that deposited on nickel plate was characterized by using SEM. The densification of coating samples was conducted at 650 °C in air. The SEM photos show the dense, uniform ( a few microns thick) LiCoO<sub>2</sub> coating on Nickel plate.

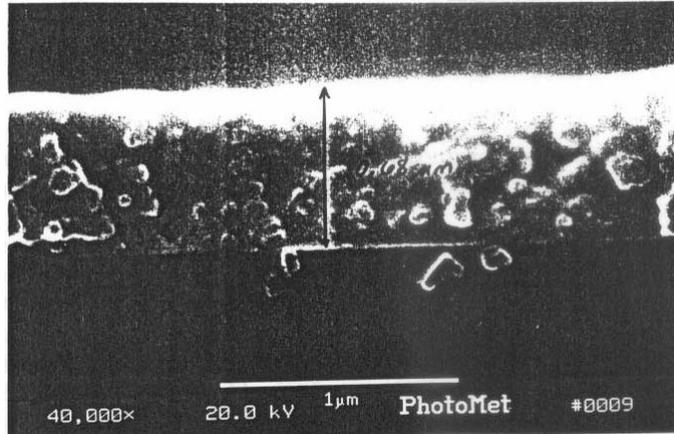


Fig. 6. SEM of LiCoO<sub>2</sub> on Ni plate

### 3.4 Evaluation of Resistance of cathode/CCC contact

*Corrosion and Ohmic Resistance:* Ohmic resistance experiments to evaluate resistance of the cathode/CCC contact is being conducted in carbonate fuel cell cathode environment . The test figure illustrated in Figure 6 is used. (62Li/38/K) CO<sub>3</sub> electrolyte is used.

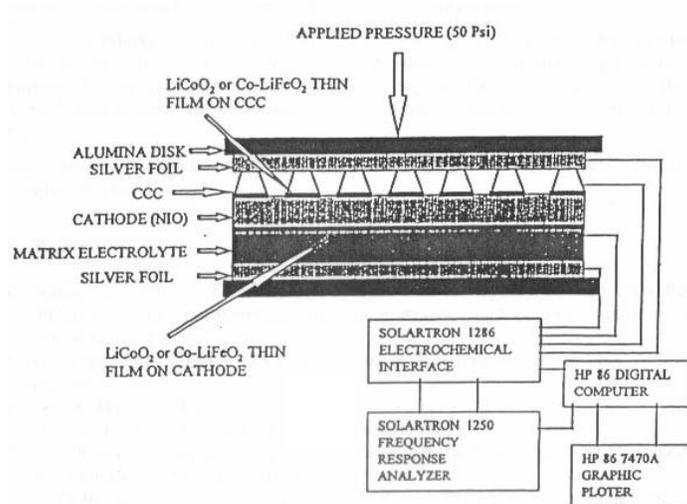


Figure 6. Experimental configuration for corrosion tests for determining corrosion and ohmic resistance of sol-gel thin film coated cathode and CCC.

The resistance is measured using AC-impedance technique. The experimental variables include film thickness, coating compositions, compressive force and aging time (100-1000hours). A similar experiment is being conducted on the components without thin film coating for comparison. The corrosion resistance of the coated CCC can also be evaluated in the above out-of-cell tests. After the test, specimens after washing by distilled water is analyzed by XRD and SEM. The amount of the thin film and cathode materials dissolved in the carbonate is determined by Atomic Absorption Spectroscopy

(AAS). A similar experiment is also conducted on the specimens without the thin film coating for comparison.

### 3.4.1. Out-of-cell Test

Out-of-cell test was conducted to evaluate Area Specific Electrical Resistance (ASR) and hot corrosion. As can be seen from Fig. 7, the resistance is stable for up to 1800 hours of testing in simulated cell environment. Electrolyte creepage loss of coated sample is reduced by nearly 1/3 (Fig. 8). Corrosion thickness in coated samples were significantly reduced from the non-coated samples (Fig. 9).

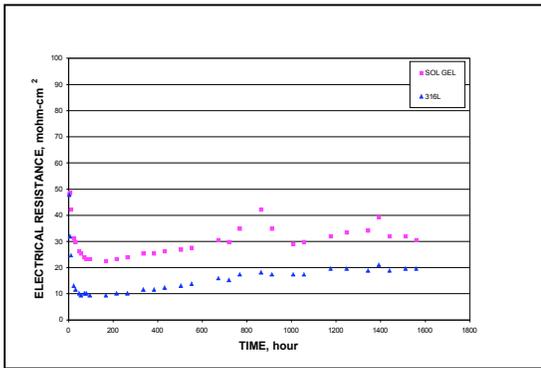


Fig. 7. The electrical resistance of coated CCC is compared with non-coated CCC. The resistance is stable for up to 1800 hours of testing.

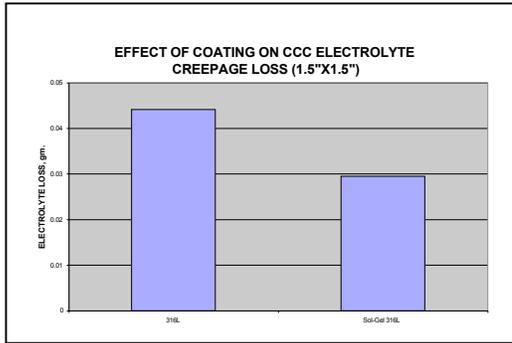
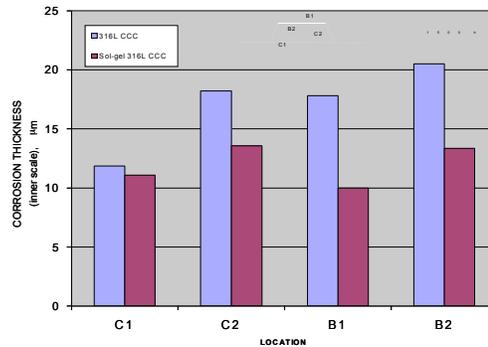


Fig. 8. Electrolyte creepage loss is reduced by nearly 1/3 due to sol-gel coating.

Fig. 9. Corrosion thickness in coated sample is significantly reduced from the non-coated one at some locations.



### 3.4.2. Single Cell Test

Single cell performance was tested in comparison of non-coated CCC. The voltage life-graph improvement was observed with coated CCC. Coated CCC did not significantly change the metal-metal contact resistance (Fig. 10). Lithium loss in the cell with coated CCC was lower than with non-coated CCC. Potassium loss exhibits a scattering data (Fig. 11).

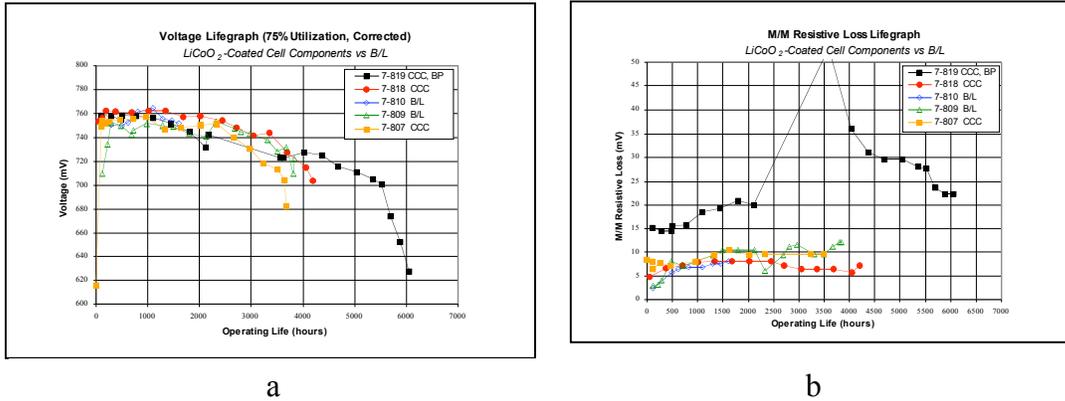


Fig. 10. Single cell performance compared with non-coated baseline. a) Open circuit voltage, b) Metal-metal contact resistance.

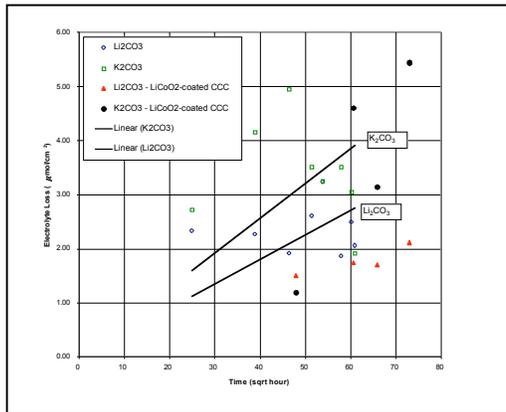


Fig. 11. Electrolyte creepage. Li loss is lower than non-coated samples. K loss exhibits a scattering data.

## IV. Conclusions and Recommendations

All the project objectives have been successfully accomplished. The feasibility of using sol-gel coating for corrosion reduction of cathode and current collector has been demonstrated. This is a key milestone in developing a low-cost, easy-to-manufacturing CCC and cathode for high temperature fuel cells. Due to the successful completion of the research, a solid foundation has been prepared for the future work.

The efforts recommended in the future work include: 1). Further development of corrosion resistant coating by optimization of composition and process parameters; 2) Further development and scaling up of coating solution and coating technology; 3). Study/testing the coatings in single fuel cell and optimize the performance of the coatings.

After successful completion of next phase work, the process will be ready for use in commercial stacks.

## **V. Feasibility Analysis**

One of the most serious problems in molten carbonate fuel cells is the corrosion of cathode current collector and lithiated NiO cathode, which has been a major lifetime-limiting factor. The research work sponsored by EISG program has proven the feasibility using Sol-gel coating to improve the corrosion protection of cathode current collector and lithiated NiO cathode. The lifetime of fuel was extended by a factor of 1.5. It is expected that the lifetime of the fuel can be further improved by increasing the thickness of the coating.

In this research, a very stable coating solution has been developed, which is important for production development of solution and coating. The coating can be deposited via dip-coating and also spray coating process. Spray process on large fuel cell components is easy to apply, low cost, and no need of expensive equipment investment, therefore is scalable.

The sintering process is conducted at low temperature (550-650°C) in air. It is also a scalable and low cost process with low energy consumption.

The coating cost is estimated at a price of less than \$1/m<sup>2</sup>. The projected the life extension is factor of 2 to 5. Therefore, this technology will greatly impact the molten carbonate fuel cells market.

## Appendix: I. References

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## **Appendix II. Proprietary Information**

### **A2.1. Preparation of coating solution**

The precursor solution was prepared by a method derived from the one previously used for the fabrication of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  coating. All the raw chemicals including lithium acetate, cobalt acetate, citric acid and ethylene glycol are purchased from Alfa/Johnson Matthey without further purifying. The procedures are as follows:

- Dissolve 11.53g of Citric acid in 30ml of ethylene glycol under the stirring till total dissolve;
- Add 6.12g of LiAc till total dissolve;
- Add 14.94g of  $\text{Co}(\text{Ac})_2$  under the stirring till total dissolve. The resultant is very stable at room temperature without precipitation in 4 weeks.

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