Title: *Batteries and Fuel Cells Working Group Report*

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Submitted to: *Notes for Workshop on Surface Processing Applications to Transportation and Utilities Technologies*

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MASTER

# Workshop on Surface Processing Applications to Transportation and Utilities Technologies
## December 10-12, 1991

### Batteries and Fuel Cells Working Group Report
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## ABSTRACT
Electrochemical energy systems are dominated by interfacial phenomena. Catalysis, corrosion, electrical and ionic contact, and wetting behavior are critical to the performance of fuel cells and batteries. Accordingly, development of processing techniques to control these surface properties is important to successful commercialization of advanced batteries and fuel cells. Many of the surface processing issues are specific to a particular electrochemical system. Therefore, the working group focused on systems that are of specific interest to DOE/Conservation and Renewable Energy. These systems addressed were:
- Polymer Electrolyte Membrane (PEM) Fuel Cells,
- Direct Methanol Oxidation (DMO) Fuel Cells, and
- Lithium/Polymer Batteries

The approach used by the working group for each of these systems was to follow the current path through the system and to identify the principal interfaces. The function of each interface was specified together with its desired properties. The degree to which surface properties limit performance in present systems was rated. Finally, the surface processing needs associated with the performance limiting interfaces were identified. This report summarizes this information.

# Workshop on Surface Processing
## Applications to Transportation and Utilities Technologies
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## Batteries and Fuel Cells Working Group Report

## I. INTRODUCTION

On December 10-12, 1991 a Workshop on Surface Processing and Applications to Transportation and Utilities Technologies was held in Dearboin, Michigan. The objectives of this workshop were to bring together knowledgeable people from academia, industry, and federally funded laboratories to form working groups in several topical areas of applied surface science, surface characterization, and surface modification. These working groups were charged with identifying and prioritizing the research needs and opportunities in their topical area. The Working Group on Batteries and Fuel Cells focused on electrochemical energy systems that are of specific interest to DOE/Conservation and Renewable Energy. The systems addressed were:
- Polymer Electrolyte Membrane (PEM) Fuel Cells,
- Direct Methanol Oxidation (DMO) Fuel Cells, and
- Lithium/Polymer Batteries.

The approach used by the working group in each of these systems was to follow the current path through the system and to identify the principal interfaces. The function of each interface was specified together with its desired properties. The degree to which surface properties limit performance in present systems was rated. Finally, the surface processing needs associated with the performance limiting interfaces were identified.

## II. POLYMER ELECTROLYTE MEMBRANE (PEM) FUEL CELLS

### A. Introduction to PEM Fuel Cells

Fuel cells offer a means of electricity production with higher efficiency and lower pollutant emission than other technologies. Basically a fuel cell converts the chemical energy in hydrogen and oxygen to electricity with water as the byproduct. The oxygen can be supplied directly as air, and the hydrogen is available from a broad range of energy resources. These include reformed organic fuels such as methanol or natural gas, reformed biomass, solar-electric driven electrolysis, wind powered electrolysis, and other renewable resources.

Phosphoric acid, molten carbonate, and solid oxide fuel cells are being developed for stationary power plant applications. However, for transportation and a broad range of other applications such as private homes and small businesses, remote site generation, and some industrial uses, compact, efficient, low/-cost fuel cells are needed.

The polymer electrolyte membrane (PEM) fuel cell has a combination of characteristics that are particularly attractive for these applications. It provides high power densities. It can tolerate $CO_2$ in the fuel stream, allowing the use of reformed organic fuel. It can be self-starting at temperatures above ~20°C. Low-cost structural materials can be used because of the low operating temperature and reduced corrosion, and the solid character of the electrolyte facilitates sealing and safety of the fuel cell stack. The limitations of the technology have been high platinum content, expensive membranes, poor carbon monoxide tolerance, water management problems, and difficulty in thermally integrating the fuel cell with a reformer. Several of these problems can be solved by modifying or improving the surface properties of the materials and components of the fuel cell.

## B. Surface Processing Aspects of PEM Fuel Cells

Figure 1 shows a generalized cross-section of a polymer electrolyte fuel cell. To emphasize the surface processing aspects, each of the elements of the fuel cell is shown separately. In real fuel cell designs, two or more of these elements may be combined in a multi-function element.
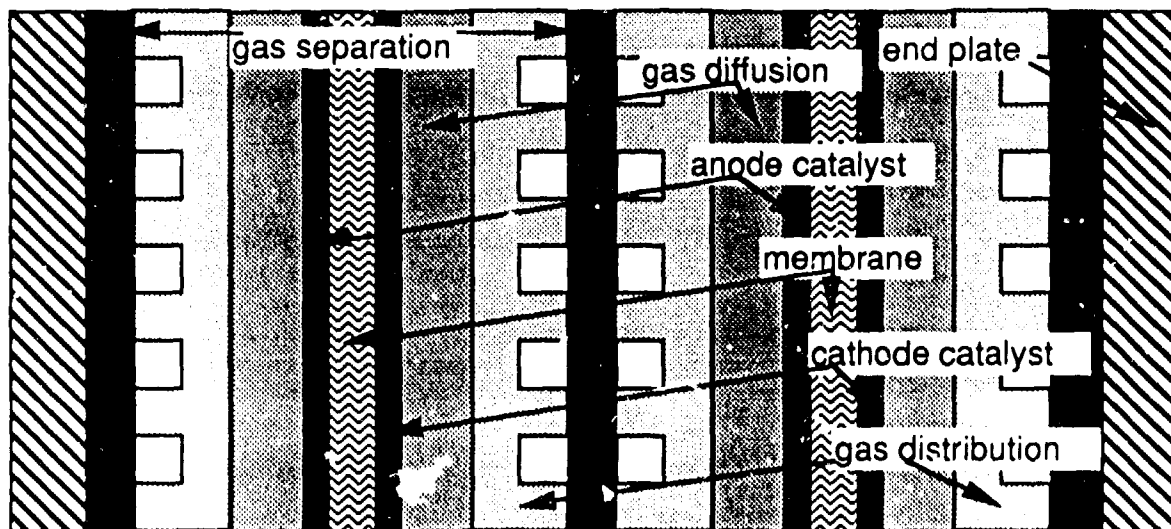


Fig.1 Schematic cross-section of a polymer electrolyte fuel cell.

In considering the surface processing aspects of the fuel cell, two classes of surfaces must be considered. The first class includes the interfaces between the elements, such as the interface between the anode and the membrane. The second class involves surfaces within an element, such as the pore surfaces within the gas diffusion structure.

The working group evaluated each of the elements shown in Fig. 1, moving from left to right. The function each element must provide was specified, and the properties that would be desired to achieve that function were identified. Each of these properties was then evaluated to determine whether the property is dominated by the surface. Finally, the importance of improving the surface properties was rated as high, medium, or low. This information is summarized in the tables below. For those interfaces which currently limit the performance of the fuel cell, suggestions for specific research and development effort are indicated.

## 1. End Plate / Gas Separator Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| mechanical compression | uniform pressure | no | low |
| | corrosion resistant | yes | low |
| electrical contact | low contact resistance | yes | low |
| | long term s'ability | yes | low |

The interface between the end plate and the gas separator does not present a significant limitation on performance.

## 2. Gas Separator / Gas Distribution Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| $H_2/O_2$ isolation | gas impermeability | possible | low |
| | corrosion resistant | yes | medium |
| electrical contact | low contact resistance | yes | low |
| | long term stability | yes | low |

note: In many designs, the function of the gas separator and the gas distribution plate are combined in a grooved impermeable plate.

Performance and design flexibility of this interface would be increased by
* development of corrosion resistant, electrically conductive coatings or
* development of surface modification for enhanced corrosion resistance.

## 3. Gas Distribution / Anode Gas Diffusion Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| gas distribution across electrode | low pressure drop | no | low |
| | good fuel utilization | no | low |
| electrical contact | low contact resistance | yes | low |
| | corrosion resistant | yes | medium |

Performance and design flexibility of this interface would be increased by
* development of corrosion resistant, electrically conductive coatings or
* development of surface modification for enhanced corrosion resistance.

## 4. Gas Diffusion / Anode Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| gas distribution across electrode | low gas diffusion resistance | possible | medium |
| | minimize $CO_2$ diffusion barrier | possible | medium |
| electrical contact to anode | good electrical contact to catalyst | yes | medium |
| | corrosion resistant | yes | medium |

Performance and design flexibility of this interface would be increased by
* improving the characterization of the interface
* modeling the gas composition within the pores as a function of operating conditions, and •
 using surface treatment to improve the electrical contact .

## 5. Anode Electrochemical Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| rapid hydrogen oxidation | high gas permeability | possible | medium |
| | good electronic contact | yes | medium |
| | good ionic contact | yes | medium |
| | high catalytic activity | yes | medium |
| | CO tolerant | yes | high |
| | resistant to other poisons | yes | high |
| | corrosion resistant | yes | medium |

note:  In a fuel cell the hydrogen is catalytically oxidized at the anode.  This reaction requires the catalytic site to be in contact with hydrogen gas, an an electrical conductor, and a hydrogen ion conductor.  In the PEM fuel cell, the hydrogen ion conductor in a hydrated ionomer.  The water content of this ionomer must be maintained over the full operating range of the fuel cell.
Moreover, the catalytic reaction is strongly affected by the water concentration at the catalytic site.
Poisoning from CO or other contaminants in reformed organic fuels is also a severe problem.

Performance and design flexibility of this interface would be increased by
- improving water transport to the catalytic sites,
- developing catalysts with improved impurity tolerance
- modeling the ionic and electronic properties of micro-porous composites,
- improving the understanding of hydrogen oxidation kinetics at ionomer/catalyst interfaces.

## 6. Anode / Ionomer Membrane Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| H$^+$ ion conduction from anode | good ionic contact | yes | medium |
| | maintain water balance at anode | possible | high |
| | long term stability | yes | low |
| prevent gas diffusion between anode and cathode | gas impermeability | possible | medium |

Performance and design flexibility of this interface would be increased by:
- determining role of membrane surface properties
- improving the control of the surface functionality by chemical surface modification
- developing an ionically conductive adhesive that could be used to bond the anode to the membrane.

## 7. Ionomer Membrane / Cathode Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| H$^+$ ion conduction to the cathode | low ionic contact resistance | yes | medium |
| | maintain water balance | possible | high |
| | prevent gas diffusion between anode and cathode | possible | medium |
| | long term stability | possible | medium |

Performance and design flexibility of this interface would be increased by:
- determining role of membrane surface properties
- improving the control of the surface functionality by chemical surface modification
- developing an ionically conductive adhesive that could be used to bond the cathode to the membrane.

## 8. Cathode Electrochemical Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| rapid oxygen reduction | high oxygen permeability | possible | medium |
| | good electronic contact | yes | medium |
| | good ionic contact | yes | medium |
| | high catalytic activity | yes | high |
| | rapid product water removal | possible | high |
| | resistant to poisons | yes | high |
| | corrosion resistant | yes | medium |

note: In a fuel cell oxygen is catalytically reduced at the cathode. This reaction requires the catalytic site to be in contact with oxygen gas, an electrical conductor, and a hydrogen ion conductor. In the PEM fuel cell, this reaction is usually the kinetically limiting reaction. Platinum or platinum alloys are the only catalysts that have been found so far that show high reaction rates in this environment. This catalytic reaction is also strongly affected by the water concentration at the catalytic site. Removal of product water from the catalytic site is critical to sustaining high performance.

Performance and design flexibility of this interface would be increased by:
- development of alternatives to platinum as an oxygen reduction catalyst.
- improving the understanding of hydrogen oxidation kinetics at ionomer/catalyst interfaces.

A DOE sponsored workshop on oxygen electrocatalysis was held October 29-November 1, 1991. Detailed recommendations for research and development on the fuel cell cathode can be found in the proceedings of that workshop.[1]

## 9. Cathode / Cathode Gas Diffusion Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| gas distribution to catalyst | rapid oxygen diffusion | possible | medium |
| electrical contact to catalyst | good electrical contact to catalyst | yes | medium |
| | corrosion resistant | yes | medium |

Performance and design flexibility of this interface would be increased by
- determination of the effects of potential cycling on corrosion of this interface,
- determination of the microscopic effects of pressure
- development of improved contact by surface treatment.

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[1] Oxygen Electrode Workshop

## 10. Cathode Gas Diffusion Layer - Internal Surfaces

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| gas distribution across electrode | low gas diffusion resistance | possible | medium |
| | $N_2$ removal | possible | medium |
| product water removal | hydrophobic | yes | medium |
| | good water droplet transport | yes | high |
| | long term stability | yes | high |

Performance and design flexibility of this component would be increased by
- improved surface treatment to maintain hydrophobicity over long periods,
- tailoring of the porosity to facilitate gas exchange,
- modeling of two phase transport in porous structures

The remaining interfaces in the PEM fuel cell on the cathode side are similar to those on the anode side with similar surface processing issues.

## C. PEM Fuel Cell Summary

The areas of improvement most needed in the PEM fuel cell are cost, water management, and impurity tolerance. Surface processing can make a contribution in each of these areas. Development of conductive, corrosion resistant coatings can reduce the cost of the structural materials. Development of processes to provide pore surfaces with hydrophobic properties that are stable over thousands of hours of operation can improve the performance and lifetime of the fuel cell. Development of catalysts with better impurity tolerance and lower cost than platinum can improve the fuel flexibility and reduce the cost of PEM fuel cells.

## III. DIRECT METHANOL OXIDATION (DMO) FUEL CELL

### A. Introduction to DMO Fuel Cells

A DMO fuel cell is fuel cell in which methan can be fed directly to an anode catalyst without the need for reforming. Although high temperature systems such as solid oxide fuel cells, operating at ~1000°C and molten carbonate fuel cells, operating at ~600°C have the potential to use methanol directly as a fuel, DMO fuel cells usually refer to relatively low temperature systems, operating at 25°C to 300°C, in which the methanol is catalytically oxidized in the presence of water to produce hydrogen ions, electrons, and carbon dioxide.

The benefits of a DMO/air fuel cell become apparent when it is compared to todays fuel processing technology. A number of approaches have been used to convert organic fuel, and in particular methanol, to a hydrogen rich fuel gas. These include high temperature reforming, low temperature reforming with selective oxidation, and low temperature internal reforming coupled with selective oxidation within the anode chamber. All of these approaches have significant drawbacks, particularly in system cost and complexity.

DMO fuel cells, in principal, eliminate the need for fuel reforming, and thus offer the potential for lower cost and a smaller power plant size. They also offer safety advantages by eliminating the need to handle hydrogen. Finally, DMO fuel cells may have better transient response than reformer based power systems. However, there are difficult problems associated with DMO fuel cells.

### B. Surface Processing Aspects of DMO Fuel Cells

In many respects the surface processing issues associated with DMO fuel cells are similar to those associated with PEM fuel cells. However, there are a set of special problems that are characteristic of DMO fuel cells that will be addressed in this section. These problems are (1) rapid poisoning of the anode catalyst by products of the methanol oxidation, such as CO and (2) methanol cross-over from the anode to the cathode which poisons the cathode catalyst.

There are two primary approaches to solving problem (1). The first is to find a catalyst that desorbs reaction products such as CO. The most promising catalysts of this type are PtRu alloys, which may have additional components. Further research to identify a superior DMO catalyst is important to development of this technology.

The second approach to solving problem (1) is to increase the operating temperature to the point where products such as CO can be thermally desorbed from the catalyst. A temperature of 200°C to 300°C would be desirable for this purpose. However, existing membrane separators are not stable at such elevated temperatures. Development of a stable membrane with high ionic conductivity would be very important to the further development of DMO fuel cells. This is primarily a materials development issue rather than a surface processing issue, but there may be surface processing aspects to fabrication of such a membrane.

Conventional membrane separators such as Nafion® are permeated by methanol, and methanol that reaches the cathode rapidly poisons the oxygen reduction reaction. One solution to this problem is to develop a membrane that is impermeable to methanol but retains the other desired properties for a fuel cell. Again, this is primarily a materials development issue; however, it may be possible to modify the surface of useful membranes to block methanol feed-through without destroying the other desirable features. This is an important line of research.

### C. DMO Fuel Cell Summary

The issues associated with the DMO fuel cell have been dealt with in great detail in a Direct Methanol Oxidation Workshop held at Georgetown University on May 14-16, 1990 The recommendations from that meeting are contained in the workshop summary.[2]

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[2] DMO workshop

# IV. LITHIUM-POLYMER BATTERIES

## A. Introduction to Lithium-Polymer Batteries

Fenton and Wright[3] observed in 1973 the remarkable conductivity of lithium salts in polyethylene oxide. Armand[4] drew attention to the practical application of these polymer electrolytes in lithium batteries. Shortly after this work, two groups - one headed by the Harwell Research Laboratories and the other headed by Hydro Quebec - were established to attempt commercialization of the technology.

In the intervening years, increased understanding of the ion conduction mechanism is the polymers has occurred. It has been realized that conduction primarily occurs in amorphous phases of the electrolytes. Simple polyethylene oxide electrolytes are sufficiently amorphous above 80°C to have conductivities above $10^{-4} \Omega^{-1} cm^{-1}$. For thin films, conductivities above $10^{-4} \Omega^{-1} cm^{-1}$ are sufficient to meet the power requirements of electric vehicle batteries. It is recognized that it is desirable to have this performance from a battery at ambient temperatures.

Recent work on the polymer electrolytes has resulted in the development of electrolytes which are amorphous at ambient temperatures and have conductivities in the range of $10^{-3} \Omega^{-1} cm^{-1}$ With this development, there is now a strong initiative to commercialize the lithium polymer battery.

Another key development, important to the lithium polymer battery, were lithium intercalating cathode materials, first proposed by Wittingham.[5] With this development "the physicists battery" was possible. In this system, the lithium moves back and forth between the cathode and anode without undergoing significant chemical reactions to new chemical entities. The electrolyte does not participate in the charge/discharge reactions and so it can be very thin, as long as it provides separation between the electrodes.

With these developments, the thin film solid state lithium battery is a reality. Typically the construction is

(1) pure lithium metal in the range of 25 μm to 50 μm thick, a graphite carbon/lithium intercalation material, or a lithium-aluminium alloy,
(2) a polymer electrolyte in the range of 50 μm to 150 μm thick, and
(3) a cathode mixture prepared from a lithium intercalating transition metal oxide powder laminated into a film of approximately 100 μm thickness.

The addition of current collectors and a sealed envelope completes the battery.

## B. Surface Processing Aspects of Lithium-Polymer Batteries

Figure 2 shows a generalized cross-section of a lithium-polymer battery. To emphasize the surface processing aspects, each of the elements of the battery is shown separately.

In considering the surface processing aspects of the battery, two classes of surfaces must be considered. The first class includes the interfaces between the layers, such as the interface between the lithium-anode and the polymer electrolyte. The second class involves interfaces within a layer, such as the interfaces between transition-metal-oxide particles and polymer electrolyte.

The working group evaluated each of the elements shown in Fig. 2, moving from left to right. The function each element must provide was specified, and the properties that would be desired to achieve that function were identified. Each of these properties was then evaluated to determine whether the property is dominated by the surface. Finally, the importance of improving the surface properties was rated as high, medium, or low. This information is summarized in the tables below. For those interfaces which currently limit the performance of the lithium battery, suggestions for specific research and development effort are indicated.

[3] D. E. Fenton,J. M. Parker, and P. V. Wright, *Polymer* 14 p 589 (1973)

[4] M. B. Armand, Polymeric Electrolytes -1, J.R. Mac Callum & K. A. Vincent Eds. Elsevier Appl. Sci. p1 (1977)

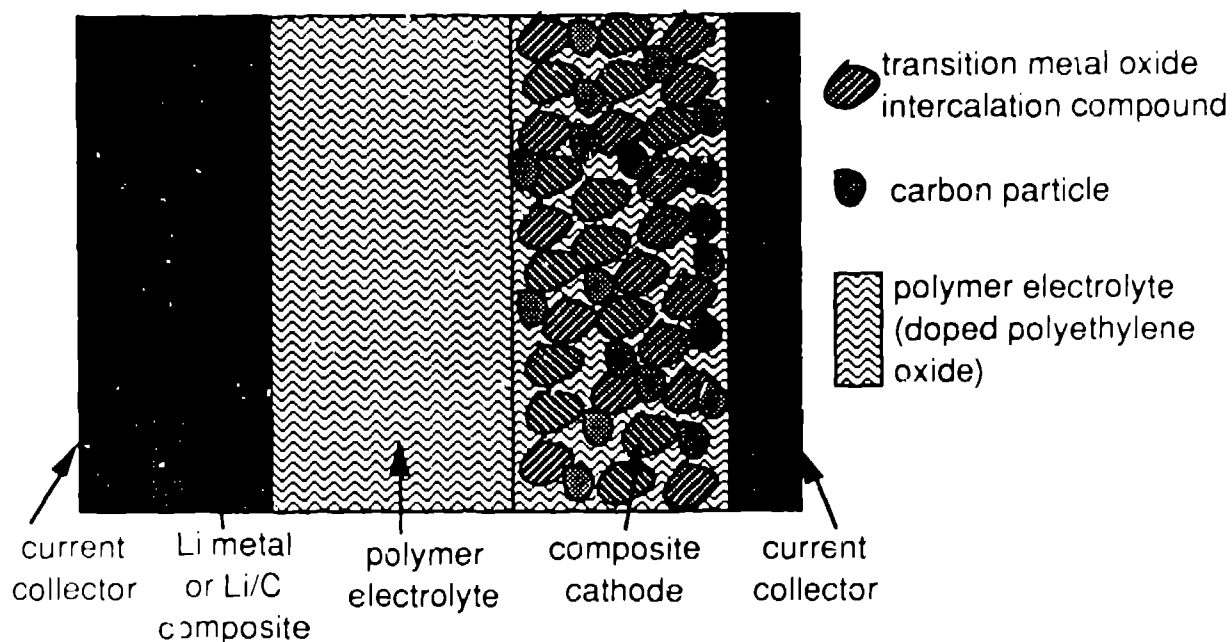[5] M. F. Whittingham, *Prog. Solid State Chem.* 12, p.41 (1978)

transition metal oxide
intercalation compound

carbon particle

polymer electrolyte
(doped polyethylene
oxide)

current
collector

Li metal
or Li/C
composite

polymer
electrolyte

composite
cathode

current
collector

Fig. 2. Schematic cross-section of a lithium polymer electrolyte battery.

## 1. Current Collector / Lithium Anode

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| electrical contact | low contact resistance | yes | low |
| | long term stability | yes | high |

The interface between the current collector and the lithium anode is subject to corrosion. Surface treatments to reduce this corrosion or processing to reduce the activity of the lithium metal would help solve this problem.

## 2 Lithium Anode / Polymer Electrolyte Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| Li$^+$ ion conduction | good ionic contact | yes | medium |
| | reversible Li deposition and stripping | yes | high |
| | long term stability | yes | high |

The long term performance of the lithium/polymer battery can deteriorate due to passivation at the Li/polymer electrolyte interface. This passivation process is not yet understood. Research is needed to identify the passivation mechanism and to develop materials techniques that will retard the passivation process.

## 3. Polymer Electrolyte / Intercalation Electrode Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| $Li^+$ ion conduction | good ionic contact | yes | medium |
| | reversible $Li^+$ insertion and withdrawal | possible | medium |
| | long term stability | yes | high |

Interfaces between the polymer electrolyte and intercalation compounds such as vanadium oxide are also affected by passivation problems. The resistance of this interface can increase by large factors over a period of a few hundred hours.[6] Research is needed to identify the passivation mechanism and to develop materials techniques that will retard the passivation process.

Another stability problem is manifested by capacity decline during cycling. This may be due to electrical isolation of some of the electrode particles in the composite caused from repeated intercalation-deintercalation cycles. The changes in particle volume during these cycles may deteriorate the interparticle contact. This problem is surface related and requires careful characterization to determine the cause. Surface processing may also provide a potential solution to this problem.

## 4. Intercalation Electrode / Current Collector Interface

| Function | Desired Properties | surface dominated | problem severity |
|---|---|---|---|
| electrical contact | low contact resistance | yes | low |
| | long term stability | yes | low |

The interface between the intercalation electrode and the current collector does not present significant surface processing problems.

## C. Lithium-Polymer Battery Summary

The key problem associated with lithium-polymer batteries is long term stability. The loss in performance can be due to passivation of internal interfaces or to corrosion. Surface analysis is an important tool to diagnose the cause of these problems, and surface processing techniques need to be developed to minimize these effects.

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[6] P. G. Bruce and F. Krok, *Electrochim. Acta*, 33, p1669 (1988)