

Abstract

The attractiveness of lithium as an anode material for secondary batteries is a topic that has received much attention throughout the battery community. However, this technology has not seen any commercial development, primarily due to the poor cycle life of lithium due to its high reactivity. Although magnesium has a lower energy density than lithium, its higher chemical stability is advantageous. When introduced to an electrolyte, active metal surfaces such as magnesium and lithium react to form a solid electrolyte interphase (SEI), consisting of byproducts which limit ionic transport which reduces the cycle life of the device. In this work we have developed coating techniques that have been applied to magnesium to hinder the formation of SEI growth. We examined the impedance spectra of cells containing magnesium electrodes and analyzed the differences of treated and untreated electrodes. Cyclic voltammetry was utilized to determine electrochemical windows of the electrolyte systems. FTIR and SEM were used to determine the chemistry of the magnesium surface and to verify existence of the coating, respectively. The impedance spectra showed that the increase in the impedance of the coated magnesium surface over time is less than that of the bare magnesium surface. FTIR spectra of both coated and bare magnesium surfaces reveal that there exists a unique surface chemistry of the coated electrode, and SEM images show that a homogeneous coating has been successfully applied. These results imply that it may be possible to prevent SEI formation on the surface of magnesium, which may be of benefit for potential use in secondary batteries.

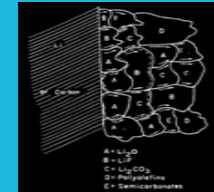


Figure 1: Lithium SEI. Peled et al. 1997

A Need for Batteries

The need for cheaper, longer lasting and more powerful batteries is rising. The intuitive choice as an anode material for a secondary battery would be lithium because of its high energy density. However, due to lithium's high reactivity and cost, we are investigating the potential use of magnesium metal as an anodic material.

	Mg	Li
Standard reduction potential vs. SHE	-2.356 V	-3.045 V
Charge capacity	2233 mAh/g	3829 mAh/g

Like lithium, the reactive magnesium surface forms a solid electrolyte interphase (SEI) when introduced to most common electrolytes. We aim to solve this problem by applying novel coating techniques previously used to inhibit SEI formation on lithium anodes¹.

Magnesium Surfaces in Different Environments

The Mg/TRGDME cell has a lower starting impedance than the Mg/PC cell, but the Mg/PC cell has a lower rate of increase in real impedance. Due to the electrochemical stability of the Mg/TRGDME system, it was used during this investigation.

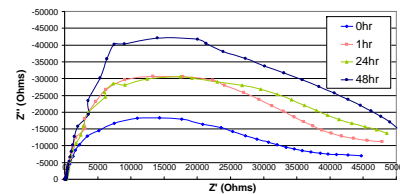


Figure 2: Impedance of magnesium metal surface exposed to TRGDME electrolyte over the course of 48 hours

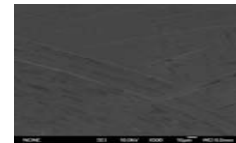


Figure 3: SEM of bare magnesium surface.

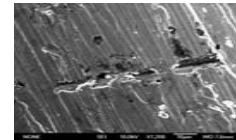


Figure 4: SEM of magnesium surface exposed to the PC electrolyte.

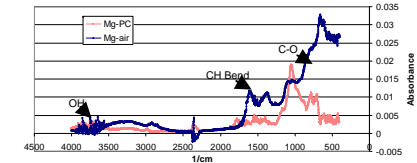
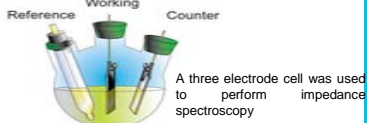


Figure 5: FTIR of bare magnesium surface and magnesium surface exposed to PC electrolyte

SEM shows that when exposed to electrolytes, the magnesium surface reacts to form an uneven layer. FTIR verifies the existence of the layer and shows the many undesired by products which the layer consists of.

Experimental Setup

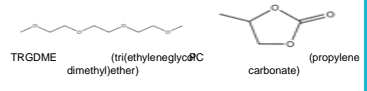
It is proposed that by coating the surface of the magnesium metal, the formation of a SEI can be inhibited.



A three electrode cell was used to perform impedance spectroscopy

Electrode material: All electrodes were constructed of magnesium metal.

Electrolyte: 0.5M Mg(ClO₄)₂ dissolved in either:



Why impedance? Since the SEI is a poor ionic conductor, impedance spectroscopy gives insight on the rate of SEI growth.

Treated vs. Untreated

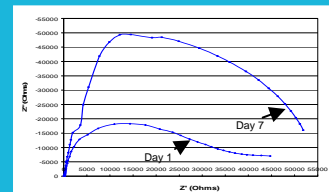


Figure 5: Impedance change over 7 days for a bare magnesium electrode in TRGDME electrolyte

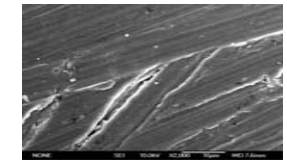


Figure 6: SEM image of magnesium exposed to TRGDME electrolyte

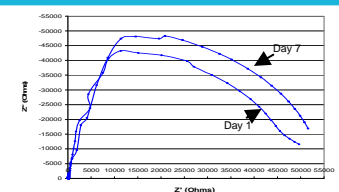


Figure 7: Impedance change over 7 days for a TMOS coated magnesium electrode in TRGDME electrolyte

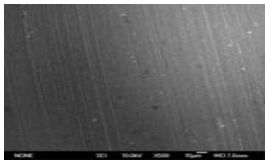


Figure 8: SEM image of TMOS coated magnesium

From the impedance data, it is obvious that there is a drastic change in change in impedance over time for the TMOS coated electrode when compared to the bare magnesium electrode. Though the initial impedance is higher for the TMOS coated electrode, the rate of impedance change is lower.

SEM images show that the TMOS coated magnesium surface is smooth and more even than that of the bare magnesium exposed to TRGDME electrolyte.

Future Directions

It is possible to slow or stop the formation of a SEI on the surface of magnesium metal. In the future, different coatings may be applied:

- Magnesium ethoxide
- Titanium isopropoxide
- Magnesium methoxide

The effect of coating times and different electrolyte systems will also be explored. This preliminary investigation shows that magnesium may be a promising anode material for rechargeable batteries.

Acknowledgements

- California NanoSystems Institute
- NSF
- UCLA NanoCER program, 2008

References

¹Marchioni, F. et al. Protection of lithium metal surfaces using chlorosilanes. *Langmuir* **23**, 11597-11602 (2007).