CARBON ENCAPSULATION OF MAGNESIUM POWDERS

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ABSTRACT

In this study, corrosion resistance of the magnesium was tried to be improved by using solvothermal encapsulation techniques to be able to use Mg and Mg based alloys in NiMH battery negative electrode compartment. For a protective encapsulating layer, sucrose and citric acid dissolved in various solvents; such as acetone, ethanol, methanol and deionized water, were used as the carbon source. Pyrolysis of the carbon sources were carried out at temperatures below the melting point of Mg. Resulting encapsulated powders were examined with several techniques to observe the morphology after encapsulation, to determine the effectivity of the encapsulating layer in alkaline environment and to see the effects of the encapsulation process on the Mg powders in terms of chemical stability. Outcomes of the study revealed that citric acid dissolved in acetone can be a better candidate than the sucrose dissolved in acetone for encapsulating layer formation in solvothermal methods, which was also verified with the results of electrical resistivity measurements and gas emission amounts of the encapsulated powders.

Keywords: Carbon encapsulation, Magnesium powder

INTRODUCTION

Magnesium is an attractive metal for a number of applications. One of these is hydrogen which can be stored in large quantities. Such hydrogen storage alloys can be used as negative electrode material in metal hydride batteries. Currently common alloy in use for this purpose is Mischmetal (rare-earth alloy) based A type of an alloy (A: Mm, La, Ce, Ti; B: Ni, Co, Mn, Al) [1]. Magnesium is even better than this alloy since the amount of hydrogen that it can store is nearly 5 times that of the current alloy [2]. However there are a number of problems to be solved if Mg is to be used as negative electrode material. These are that MgH2 is too stable for such purposes and it needs to be destabilized, kinetics of hydrogenation and dehydrogenation needs to be accelerated [3].

There is one additional problem which is common to Mg and Mg based alloys. Environment in metal hydride batteries is alkaline and Mg is subject to corrosion in this environment. Thus if Mg and Mg based alloys are to be used as negative electrode material, they need to be protected from this environment. The current study concentrates on this problem and examines the possibility of protecting Mg with carbon encapsulation.

EXPERIMENTAL PROCEDURE

Mg powders used were -325 mesh (Alfa Aesar, 99.8%) which were coated with carbon via a solvothermal method. Two agents were used in the encapsulation; sucrose (Sigma-Aldrich, <99.5) and citric acid (Sigma-Aldrich, <99.5).

The method with sucrose is as follows. The sucrose was dissolved in in a suitable solution (ethanol, methanol, acetone, deionized water). The solution was mixed with Mg powder keeping Mg:C = 95:5. After the partial vaporization of the solution, a gel-like mixture was obtained. This gel placed into a tube furnace and heated to the 300 °C with a rate of 5 °C/min. for pyrolysis. This was carried out under nitrogen flow (8 slph) so as to prevent oxidation and remove the by-products of the pyrolysis from the furnace atmosphere.

In the second set of experiments sucrose was replaced with citric acid, the other details were the same as above.

The resulting encapsulated powders were characterized with SEM (JEOL JSM6400) so as to observe the morphology of encapsulation. Encapsulated powders were also examined with Raman spectroscopy (Bruker IFS 66/5) as well as with X-ray diffraction (Rigaku DMAX 2200).

The extent to which encapsulated powders were resistant to corrosion was examined with a set-up given in Fig.1. Here the set-up consist of an Erlenmeyer flask of 250 ml. connected to a volumetric gas collecting cylinder. A typically 2.5 g. of encapsulated powder was placed at the bottom of the flask. The experiment was started by pouring 100 ml. 6M KOH into it. This is expected to
produce hydrogen gas, according to the reaction provided below (Equation 1);

\[ Mg + H_2O \rightarrow Mg(OH)_2 + H_2 \]  

(1)

The amount of gas (H\textsubscript{2}) evolved was measured with in the cylinder, after 24 hours.

Encapsulated powders were also characterized with regard to their resistivity. For this purpose encapsulated powders were poured into a die and pressed into a pellet, 18 mm diameter and 0.5 mm in thickness by single action pressing.

Resistivity values were calculated from the resistance measured with a homemade four-point-probe tester. The measuring probes were coated with gold to minimize errors due to the internal resistance of the probe needles. The distance between the testing probes were 4 mm since in case of higher sample thicknesses than the 40% of the inter-probe distance, resistance cannot be measured correctly [4]. Measurements were carried out at room temperature and the resistance, \( R \), obtained from samples were converted into resistivity, \( \rho \) using the relation;

\[ \rho = 2\pi sF R \]  

(2)

where \( s \) is the inter-probe distance (m) and \( F \) is the correction factor (0.81) for the sample geometry.

### RESULTS AND DISCUSSION

Initial experiments were carried with sucrose-acetone. Three different temperatures were employed; 400 °C, 350 and 300 °C heating rate being the same in all experiments. It was noticed that Mg vaporizes at 400 °C and to be on the safe side, 300 °C was selected as pyrolysis temperature. Next a number of experiments were carried with different pyrolysis time; 4, 6, 8, 10 hours. After 8
hours of pyrolysis, the mixture was fully hardened and powders could not be regained. Therefore pyrolysis was carried out for 6 hours.

A typical SEM image of Mg and encapsulated Mg powders is given in Fig.2. Here Mg encapsulated with sucrose-acetone appears quite satisfactory, Fig.2 (b) in terms of appearance, but it charges heavily under SEM implying that it is not conductive enough. In addition to the charging problem, organic traces due to the incomplete pyrolysis were also detected in the SEM images of the sucrose-acetone used encapsulation route.

In order to obtain more satisfactory coating, following the studies\cite{5,6}, sucrose was replaced with citric acid. Since the solubility of citric acid in acetone is rather small, alternative solvents, namely methanol, ethanol and deionized water were used. Unfortunately all of these solvents, led to oxidation of Mg (see Fig.3). Therefore the original solvent, acetone, was continued to be used and limited solubility was overcome by the use of excess solvent.

![Figure 3. X-ray spectrum of the encapsulated powders by using citric acid and ethanol. Rietveld analysis conducted on the powders revealed that the amount of MgO formed is 19.1% at. (Bragg R-factor: 7.8, reduced \( \chi^2 \): 7.8)](image)

An example of Mg powders encapsulated with citric acid-acetone is given in Fig.2 (c). The sample charges very little indicating that it has better conductivity as compared to previous samples. Also powders have the same appearances as the initial powder compare Fig.2 (c) with Fig 2 (a).

Results of corrosion experiments are given in Table 1. This table comprises values referred to gas collected from powders coated with sucrose-acetone and citric acid-acetone routes. Pure Mg was also included for comparison. As seen in the table Mg encapsulated with sucrose-acetone route produces 24 ml. \( \text{H}_2 \) gas within 24 hours. Pure Mg produces \( \text{H}_2 \) which larger than the capacity of the measuring cylinder (> 80 ml.). The best result was obtained with Mg powder encapsulated with citric acid-acetone route. The value was one fourth of that collected with sucrose-acetone route, i.e. 6 ml. gas collected after the 24 hours of exposure to the 6M KOH solution.

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount of gas collected (ml.)</th>
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<tbody>
<tr>
<td>Mg</td>
<td>&gt; 80</td>
</tr>
<tr>
<td>Mg - Sucrose @Acetone</td>
<td>≈ 24</td>
</tr>
<tr>
<td>Mg - Citric Acid @Acetone</td>
<td>≈ 6</td>
</tr>
</tbody>
</table>

Resistivity values obtained for the samples at room temperature are given in Table 2. It should be noted that the resistivity values in sucrose route is 3 orders of magnitude larger than those obtained with citric acid route. Thus resistivity measurements also implies that the coating has a better conductivity with citric acid.

Mg encapsulated via citric acid route was also examined with Raman spectroscopy. The spectrum recorded is given in Fig. 4. The spectrum, despite pyrolysis still shows the bonds other than C-C e.g. C-H which implies that the pyrolysis is not yet complete.
Figure 4. Raman spectrum of the encapsulated Mg with citric acid-acetone in comparison with the carbon. Peaks labeled at carbon represents the D band (1336 cm$^{-1}$), G band (1568 cm$^{-1}$) and 2D band (2660 cm$^{-1}$), respectively, which should be clearly resolved in an appropriately pyrolyzed sample having a carbon based encapsulation layer.

Table 2. Resistivity (in nΩ·m) data of the Mg, Mg encapsulated with sucrose and Mg encapsulated with citric acid samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrical Resistivity (nΩ·m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>105.9</td>
</tr>
<tr>
<td>Mg - Sucrose @Acetone</td>
<td>27.8×10$^3$</td>
</tr>
<tr>
<td>Mg - Citric Acid @Acetone</td>
<td>759.1</td>
</tr>
</tbody>
</table>

CONCLUSION

In the current work, for the purpose of preventing the corrosion in alkaline environment, Mg powders were encapsulated with a solvothermal method. The study has shown the following:

1. Mg powder can be encapsulated with sucrose or citric acid using acetone as a solvent.

2. The use of other solvents such as ethanol, methanol or deionized water is not recommended as a solvent because they tend to oxide Mg powder.

3. Of the two routes, citric acid is a better encapsulating agent as it provides a better protection of Mg as verified by gas collecting experiments and resistivity measurements.

Lastly, it should be mentioned that even with citric acid Mg could not be fully protected as there is still H$_2$ gas evolution as it contacts with KOH solution. This is consistent with Raman measurement which implies that the pyrolysis is not complete at 300 °C. The use of a higher pyrolysis temperature, e.g. 350 °C, maybe recommended for a better encapsulation.

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