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Generation of highly porous Li–Mg and Li–Zn alloys from kinetically controlled lithiation

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ABSTRACT

Li–Mg and Li–Zn alloy electrodes are prepared by the kinetically controlled vapour deposition (KCVD) of Li–Mg and Li–Zn alloys on a temperature-controlled substrate. The mode of preparation greatly influences the microstructure, surface morphology and electrochemical properties of these Li–Mg and Li–Zn alloys. The KCVD technique, as applied to the generation of Li–Mg alloys, establishes the composition of each prepared alloy by independently varying the temperature of the molten lithium, the temperature of a solid magnesium surface with which the lithium interacts, and the temperature of the substrate on which a resulting intimately mixed Li–Mg mixture is deposited. Here, the required temperature for lithium induced magnesium vaporization is more than 200°C below the magnesium melting point. The effect of variable temperature control on the microstructure, morphology and electrochemical properties of the vapour-deposited alloys has been studied and the diffusion coefficients for lithium in the Li–Mg alloy electrodes prepared by the KCVD method are found to be in the range 1.2–5.2 × 10⁻⁹ cm²/s⁻¹ at room temperature. The diffusion coefficients for moderate lithium content alloys, firstly, exceed those for standard alloy preparation and, secondly, are two to three orders of magnitude larger than those for other lithium alloy systems (e.g. 6.0 × 10⁻¹⁰ cm²/s⁻¹ in LiAl). A variant of the KCVD technique is used to generate highly porous Li–Zn alloy films prepared by controlling the temperature of a molten lithium source and the rate at which a zinc source, placed in proximity to the lithium, equilibrates in temperature as the lithium interacts with the zinc. Diffusion coefficients for the Li–Zn alloy electrodes prepared by this variant of the KCVD method vary from 10⁻⁷ to 10⁻⁹ cm²/s⁻¹ at room temperature, depending on the alloy composition. This should be compared with the standard alloy whose diffusion coefficient never exceeds 10⁻⁹ cm²/s⁻¹ for any composition. These observations suggest that alloys generated using kinetically controlled lithiation display an enhanced porosity and diffusivity useful for a number of applications.

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§ 1. Introduction

Although various lithium alloys have been studied for high temperature Li/Fe$_2$S systems (Anani and Huggins 1992), few studies have been performed on lithium alloy electrodes with the goal of producing ambient-temperature batteries. This is somewhat surprising since the diffusivities of lithiated carbon electrodes (of the order of $10^{-8}$–$10^{-9}$ cm$^2$ s$^{-1}$ for Li$_x$C$_6$ at 25°C and decreasing with increasing $x$ (Guyomard and Tarascon, 1992)) can be starkly contrasted to lithium alloy diffusivities which are notably higher (for Li$_x$Si$_3$ at 25°C it is $(3-5) \times 10^{-7}$ cm$^2$ s$^{-1}$ (Wang et al. 1986)). The reported diffusivity of lithium in the $\beta$ phase of a Li–Mg alloy at 420°C is about $(1.8-5) \times 10^{-6}$ cm$^2$ s$^{-1}$ (Iwadate et al., 1987), suggesting a significant diffusivity at room temperature which we have confirmed in this study. These high diffusivities might prove useful in alleviating the dendrite formation which tends to plague lithium-based batteries. Further, an increased diffusivity, created through the application of novel deposition techniques, may prove useful in several additional applications.

The simplest method to prepare a binary alloy requires that one carefully heats two metals, which, when in contact, can be combined to form the desired composition of a product alloy at a predetermined temperature. However, usually it is necessary to operate at temperatures necessary to melt both metals and it is difficult to control the microstructure and morphology of the obtained alloy. As an alternative to this approach, we have previously developed a system (Dudel et al., 1997) to produce lithium alloy films using several variants of the physical vapour deposition process.

Kinetically controlled lithiation was developed for the preparation of Li–Mg and other alloys with controlled microstructure including grain size, orientation, composition and porosity. The overall system, discussed in more detail elsewhere (Dudel et al., 1997), operates at $10^{-6}$ Torr and relies on the combination of a series of simple and inexpensive interlocking containment devices and configurations, each of which may possess independent temperature control, designed to promote lithium vapour interactions, forming alloys of the elements soluble in lithium (e.g. magnesium, zinc, tin, lead, copper, silver and silicon). The individually heated metal sources are coordinated with a substrate for film deposition, all under virtually independent temperature control.

In a configuration in which lithium vapour is made to interact with an independently heated magnesium disc or with a zinc disc whose temperature is determined by the development of a thermal equilibrium with the lithium vapour, it is possible to promote (Dudel et al. 1997) the intimate mixing and simultaneous vapour deposition of magnesium or zinc and lithium on to a substrate to form a desired Mg–Li or Zn–Li alloy. For the Li–Mg system this process can be initiated at temperatures some 200°C below the melting point of magnesium (Dudel et al., 1997). The presence of lithium vapour, after promoting the removal of a magnesium oxide coating, appears to increase the vapour pressure of the surface magnesium metal and, as a result, facilitates the intimate mixing of magnesium and lithium vapours. A similar process may be operative for the zinc system, albeit at a lower temperature.

The control of deposition and uniformity of composition clearly distinguishes the processes that we consider from an expensive and lengthy co-deposition using two beams from, for example, independently heated magnesium and lithium sources (Bakshi et al. 1985). By independently controlling the temperature of the molten
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lithium and solid magnesium, films of specific composition can be fabricated. To obtain similar results, a slightly different procedure is followed for the zinc system. The temperature of the alloy deposition substrate can also be varied to control the morphology of the grain structure of the vapour deposited alloy film, introducing a significant porosity. Deposition rates are sufficient (e.g. 0.04 in h⁻¹ or greater for the Li–Mg system) (Dudel et al. 1997) so as to create rapidly the desired alloy films. Consequently, the kinetically controlled vapour deposition (KCVD) technique provides an efficient and inexpensive method to fabricate porous lithium-based films, of which the Li–Mg and Li–Zn alloy systems are representative, over a wide range of desired compositions. Under these conditions, the bulk diffusivity should be coupled with a significantly enhanced surface diffusion owing to the formation of Li–Mg or Li–Zn alloys with highly porous structures controlled by the kinetically based production process (Dudel et al. 1997). As a result, the diffusion of lithium in alloy should be sufficiently fast that the activity of lithium at an electrode interface will remain less than unity avoiding lithium dendrite formation during cycling. In this paper, we report our findings as we evaluate the porosity and diffusivity of select KCVD-formed Li–Mg and Li–Zn alloys at room temperature.

§2. EXPERIMENTAL DETAILS

Magnesium rod stock (diameter, 1 in; purity, greater than 98%) was purchased from A. D. Mackey, zinc rod (purity 99.99+ %) and lithium rod (purity, greater than 98%) were purchased from Alfa Inorganics.

The configuration used for the KCVD process, as depicted in figure 1, represents an improved modification of our previous design (Dudel et al. 1997). Here, in one manifestation of the design, lithium vapour, heated in a lower ‘crucible’ (thermal coaxial heating element (Phillips)) can be made to interact with an independently heated magnesium disc (cut from 1 in rod stock, A. D. Mackay) promoting the controlled liberation of magnesium at temperatures far below its melting point, 651°C. The magnesium disc is mounted on a second thermal coaxial heating element. When forming a Li–Mg alloy, a magnesium metal disc–0.005 in tantalum sheet–heating coil–thermocouple configuration is suspended inside the intermediate containment vessel as indicated in figure 1. The lithium vapour interacts with the magnesium metal and is mixed with the resulting vaporizing magnesium. This configuration facilitates the intimate mixing of magnesium and lithium vapour and promotes the simultaneous vapour deposition of a controlled and intimately mixed magnesium and lithium concentration on to a temperature-controlled substrate in the upper crucible region to form the desired Li–Mg alloy. The method is to be contrasted with Li–Mg vapour deposition systems where separate sources are used for each metal in the alloy.

The outside of the lower lithium-containing vessel is wrapped in a thermal coaxial heating element (Phillips) and is usually heated to temperatures exceeding 500°C. Lithium (Fisher Scientific; purity, greater than 98%; melting point, 179°C) placed in the bottom of this container is melted as the container temperature is monitored by a thermocouple (Omega type K) again placed directly next to the thermal coaxial heating element. Again for Li–Mg alloy formation the magnesium and lithium are maintained at two different temperatures (table 1) using the two control loops of an Omega CN3000 temperature controller. The lithium vapour pressure at the temperature of these experiments ranges from about 10⁻³ to 10⁻² Torr.
The unique process leading to alloy formation results in the creation of a substantial magnesium vapour concentration at temperatures of nearly 200°C (table 1) below the magnesium melting temperature and is facilitated by the interaction of lithium vapour with the solid magnesium disk (Dudel et al. 1997). The interlocking containment vessels in figure 1 are constructed from type 304 stainless steel. The upper chamber houses the substrates on which the intimate mix of lithium and magnesium can be deposited both on a tantalum sheet held in place next to a water or dry ice-methanol slush-bath-cooled top plate or on a tantalum sheet which sheaths and is intimately connected to the inner side walls of the upper chamber. The composition of the deposited alloy can be controlled by independently adjusting the magnesium and lithium temperatures. Diffusion coefficients exceed those for direct alloy formation (table 2).

Table 1. Summary of representative experimental conditions for Li–Mg alloy formation using the KCVD method and diffusivity of Li in the alloys as determined using chronoamperometry

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg temperature (°C)</th>
<th>Li temperature (°C)</th>
<th>Substrate temperature (°C)</th>
<th>Diffusion coefficient ($10^{-7}$ cm² s⁻¹)</th>
<th>Alloy's Li content (mole% (wt%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>525</td>
<td>625</td>
<td>≈30</td>
<td>1.22</td>
<td>12 (5.3)</td>
</tr>
<tr>
<td>2</td>
<td>485</td>
<td>635</td>
<td>≈30</td>
<td>1.8</td>
<td>12 (5.5)</td>
</tr>
<tr>
<td>3</td>
<td>485</td>
<td>635</td>
<td>≈15</td>
<td>3.91</td>
<td>20 (7.8)</td>
</tr>
<tr>
<td>4</td>
<td>460</td>
<td>650</td>
<td>≈15</td>
<td>5.17</td>
<td>25 (9.4)</td>
</tr>
</tbody>
</table>
Table 2. Diffusion coefficients of lithium in Li–Mg alloys prepared by the direct-alloying method.

<table>
<thead>
<tr>
<th>Li–Mg composition (mol%)</th>
<th>Diffusion coefficient (10^{-8} \text{ cm}^2 \text{ s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>90–10</td>
<td>9.89</td>
</tr>
<tr>
<td>80–20</td>
<td>5.06</td>
</tr>
<tr>
<td>70–30</td>
<td>3.95</td>
</tr>
<tr>
<td>60–40</td>
<td>2.46</td>
</tr>
</tbody>
</table>

To prepare the Li–Zn alloys, a variant of the approach for the Li–Mg system was used. Here a zinc disc replaces the magnesium disk, however, the zinc is no longer independently heated and obtains its temperature through thermal and radiative equilibration with the lower lithium crucible. The data in table 3 summarize the appropriate parameters.

By virtue of the manner in which the magnesium and zinc vapors are formed and mixed with lithium vapour, the alloy subsequently deposited on the temperature-controlled substrate can be shown to have a nearly uniform composition. The control of deposition and uniformity of composition clearly distinguish the process from a codeposition using two beams from independently heated metal sources. The microstructure and surface morphology of the Li–Mg and Li–Zn alloys were characterized using a scanning electron microscope (Hitachi S-800) and the lithium contents (weight percentages) of the alloys were determined using inductively coupled plasma atomic absorption spectroscopy.

A three-electrode cell was employed for electrochemical measurements in this work. The reference electrode and counter-electrode were made of lithium foil and 1 M LiN(SO₂CF₃)₂ in EC/DMC (1:2 by volume) solution was used as the electrolyte. The apparent surface area of the alloy electrodes is 0.2 cm². Two layers of Celgard 2400 film were chosen as the separators. The EC and DMC were dried for at least 24 h with activated 4A molecular sieves. Cyclic voltammetry and chronoamperometry were performed using a Solatron 1285 system controlled using a personal computer.

§3. Results

3.1. Diffusion coefficient of lithium in Li–Mg and Li–Zn alloys

For most applications including lithium battery electrodes, the microstructure of the alloy must facilitate the efficient transport of lithium away from, for example, the electrode–electrolyte interface (into the alloy) at a sufficiently fast rate. The factor that controls this process is the diffusion of lithium in alloy. It is well known that the diffusion process of lithium atoms in a lithium alloy is the rate-determining step when lithium atoms intercalate into alloy. Therefore, it is important to determine the lithium diffusion coefficient in these alloys and to assess whether the KCVD technique provides a significant increase in this diffusion relative to standard alloy generating techniques. A potentiostatic transient method, chronoamperometry, was used to determine the diffusion coefficient of lithium atoms in the solid Li–Mg and Li–Zn alloys (Wen et al. 1981; Machill and Rahner 1995, 1997).
When the potential of an alloy electrode (with respect to a lithium reference electrode) is stepped from open-circuit voltage to a value sufficiently positive (e.g. 0.65 V) that the cell current is completely controlled by the diffusion of lithium out of the Li–Mg or Li–Zn alloy, the diffusion process inside the solid alloy, the observed current decays according to the Cottrell equation (Wen et al. 1981, Machill and Rahner 1995, 1997):

$$I(t) = \frac{zFS(c^*_L - c_L)}{\frac{D_L}{\pi t}}$$

where $z$ is the charge number of the electroactive species (lithium atoms) in the electrolyte phase, $F$ is the Faraday constant, $S$ is the active surface area of the electrode, $D_L$ is the diffusion coefficient of lithium in a Li–Mg or Li–Zn electrode, $c_L$ is the lithium concentration at the surface of the Li–Mg or Li–Zn alloy electrode and $c^*_L$ is the initial uniform concentration of lithium in the alloy. The diffusion coefficient $D_L$ can be determined from the slope of a linear plot of $I$ versus $t^{-1/2}$. A typical chronoamperogram ($i$ versus $t$) for the sample 1 Li–Mg alloy listed in table 1 is depicted in figure 2(a) and the relationship between $i$ and $t^{-1/2}$ is presented in figure 2(b).

![Figure 2](image-url)

Figure 2. (a) A typical chronoamperogram of a Li–Mg alloy electrode in 1 M LiN(CF$_3$SO$_2$)$_2$ in EC/DMC (1:2 by volume). The potential was stepped from an open-circuit voltage of 0.026 V to 0.65 V (versus Li$^+$/Li), and kept at 0.65 V for 20 s. (b) Cottrell relationship $i \propto t^{-1/2}$, based on the data shown in (a).
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3.2. Microstructure and surface morphology of Li-Mg alloys prepared by kinetically controlled vapour deposition

The composition, microstructure and morphology of Li-Mg alloy films produced by the KCVD method under different preparation conditions have been systematically studied through independent variation in the temperature of the magnesium and lithium sources, and of the Li-Mg alloy deposition substrate (Dudel et al. 1997). The lithium content in the Li-Mg alloy film can be changed from 0.08 to 30 wt% when the temperature of the lithium is varied from about 405 to 675°C and the temperature of magnesium, at an optimal temperature, remains in the approximate range 425–485°C, depending on the precise containment vessel configuration used to carry out the deposition process. Generally, the higher the temperature of the lithium metal, the higher is the lithium content in the alloy film. The microstructure and morphology of the Li-Mg alloy films are mainly determined by the substrate temperature. When the substrate temperature is lowered, the microstructure of a deposited Li-Mg alloy film can be made to transform from the cubic crystalline structure characteristic of a phase-equilibrated Li-Mg alloy (with greater than 26 wt% Li) to a fibrous columnar microstructure and, on further cooling, to a tapered columnar microstructure with extensive voids (Dudel et al. 1997), as the film transforms from a dense to a porous structure. For applications related to lithium batteries, this porous structure is preferred. In addition, based on the experience that we have acquired in handling directly formed Li-Mg alloys, we find that the hardness of an alloy whose magnesium content is in excess of 40 mol% (about 70 wt%) renders the alloy difficult to manipulate (Shi et al. 2000b). Therefore it is desirable to employ higher-lithium-content Li-Mg alloy films which also display a corresponding porous structure as the preparation conditions for the Li-Mg alloy films are chosen at sufficiently high lithium temperatures and low substrate temperatures. The data in table 1, however, are for moderate-lithium-content alloys.

The scanning electron micrographs shown in figures 3 (a) and (b) and figures 3 (c) and (d) correspond to a cross-sectional view of four Li-Mg alloy samples of moderate lithium contents deposited on a tantalum substrate (table 1) at about 30°C and about 15°C respectively. All the samples display a columnar and porous structure. For battery applications this porous structure is beneficial to the passage of liquid electrolyte into the pores, therefore increasing the real contact area between a liquid electrolyte and a Li-Mg alloy anode electrode surface. Specifically, under selected conditions (e.g. lithium temperature of 650°C, magnesium temperature of 460°C and tantalum substrate temperature of 15°C), the obtained alloy (samples 3 and 4) possesses a substantially porous structure (figures 3 (c) and (d)). In fact, the scanning electron micrographs taken in top view demonstrate that the morphology of the deposited alloy films varies significantly as a function of substrate temperature (figure 4). When the substrate temperature is 30°C, the surface of the alloy film appears to be relatively dense, displaying a block-like structure (figures 4 (a) and (b)). A striking change in the surface morphology of the alloy films (figures 4 (c) and (d)) is apparent at the lower substrate temperature, 15°C, as dry ice cooling is used to adjust the temperature of the substrate. These latter samples consist of highly porous surfaces constituted of fine particles. They clearly have a large real surface area which can facilitate the transport of liquid electrolyte into a Li-Mg alloy electrode.
Figure 3. Scanning electron micrographs of cross-sectional views of Li–Mg alloys prepared by the KCVD technique under the conditions specified in table 1: (a) sample 1; (b) sample 2; (c) sample 3; (d) sample 4.
Table 1 demonstrates, firstly, that the diffusion coefficients for Li–Mg alloys prepared by the KCVD method are all in the $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ range and, secondly, that they increase significantly with the apparent porosities of the samples. They should be compared with the diffusion coefficients for Li–Mg alloys prepared by the direct alloying method. In table 2 we present these data for four Li–Mg composi-
Figure 4. Scanning electron micrographs of the top views of the Li–Mg alloys prepared by the KCVD technique under the conditions specified in table 1: (a) sample 1, (b) sample 2; (c) sample 3; (d) sample 4.
Highly porous Li–Mg and Li–Zn alloys

Figure 4. (Continued)
tions. It should be apparent that the alloys prepared by the KCVD method have diffusion coefficients which are an order of magnitude greater than those prepared via the standard mixing techniques.

3.3. Microstructure and surface morphology of Li–Zn alloys prepared by kinetically controlled vapour deposition

The scanning electron micrograph shown in figure 5 corresponds to that for a Li–Zn alloy sample deposited on a tantalum substrate. In contrast with the Li–Mg alloys prepared by KCVD (Dude1 et al. 1997, Shi et al. 2000b), this Li–Zn sample (table 3) does not display a columnar or a tapered structure. Instead, it consists of aggregated particles while displaying a very porous structure. If the alloy film is used as an anode in lithium batteries, this porous structure is beneficial to the passage of liquid electrolyte into the pores as, for example, one increases the real contact area between the liquid electrolyte and the Li–Zn alloy electrode surface. When the preparation of the Li–Zn alloy allows for the near equilibration of the lithium and zinc temperatures following each temperature rise of the lithium source, the surface of the produced alloy film appears relatively dense, displaying a block-like structure. In contrast with the Li–Mg alloys, the composition of the obtained Li–Zn alloy is in

![Figure 5. Scanning electron micrograph corresponding to (a) the cross-sectional and (b) the top view of a Li–Zn alloy prepared by the KCVD technique at a substrate temperature of 30°C.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn maximum temperature (°C)</th>
<th>Li maximum temperature (°C)</th>
<th>Substrate temperature (°C)</th>
<th>Li content in Li–Zn alloy (mol% (wt%))</th>
<th>Diffusion coefficient (10⁻⁸ cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>376</td>
<td>550</td>
<td>20</td>
<td>≈ 90 (≈ 50)</td>
<td>≈ 4.8</td>
</tr>
</tbody>
</table>
large part determined by the temperature and equilibration of the lithium and zinc sources although the substrate temperature also plays a role. Chronoamperometry suggests that the lithium diffusion coefficient for this alloy generated using the KCVD technique can fall in the low 10^{-7} \text{ cm}^2 \text{s}^{-1} range but can vary with composition to a value approaching 10^{-9} \text{ cm}^2 \text{s}^{-1}. This should be contrasted with a maximum diffusion coefficient of 10^{-9} \text{ cm}^2 \text{s}^{-1} for a Li-Zn alloy prepared in the standard fashion (Fujieda et al. 1992). The electrochemical behaviour of the prepared Li-Zn alloy electrodes, as studied using cyclic voltammetry, is discussed in detail elsewhere (Shi et al. 2000a).

§4. DISCUSSION

The measured diffusion coefficients for the Li-Mg and Li-Zn alloys prepared by the KCVD method suggest that the diffusivity of lithium in these alloys, firstly, exceeds that for the alloys prepared by standard techniques and, secondly, is much greater than those of other intercalation electrode materials. It appears that the KCVD process is a useful alloy-generating technique; it has the ability to modify the microstructure and morphology of alloy electrodes through reactant mixing and substrate temperature control. Not only might the Li-Mg system, whose morphology can be modified through generation on a substrate at room or even lower temperature, provide a means to obviate the problem of lithium dendrite formation during the cycling of lithium based batteries, but also the high capacity possible for a Li-Mg alloy electrode (642 mA g^{-1} when it is cycled from Li_{4}Mg_{6} to Li_{6}Mg_{4}) might considerably exceed that of currently accessible lithiated carbon electrodes. The optimization of these materials for battery electrodes and the long-term reversibility of the Li-Mg high-capacity electrode are under investigation and will be reported in subsequent communications.

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