

Short communication

Enhancement of the rate capability and cyclability of an Mg–C composite electrode for Li secondary batteries

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Abstract

An Mg–C composite, prepared by high energy mechanical milling, was investigated as an anode material for lithium-ion batteries. Electrochemical tests demonstrated that the first charge and discharge capacities were 1810 and 1433 mA h g⁻¹, respectively, with a coulombic efficiency for the first cycle of 80%. Ex situ XRD analyses combined with a differential capacity plot of the Mg–C composite electrode showed the phase changes during the electrochemical Li–Mg alloying/dealloying reaction. Significantly enhanced rate capability and reversibility of the electrochemical reaction of Mg with lithium were observed and the improvement in the electrochemical properties of the composite electrode was attributed to the high energy mechanical milling of Mg with carbon on the surface of the Mg–C composite.

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1. Introduction

Lithium-ion secondary batteries are currently used as portable power sources in the consumer electronic market. Along with the rapid progress, which has been made in electronic devices, intensive research has been conducted to increase the energy density of lithium-ion batteries. Efforts to raise their gravimetric and volumetric energy densities have made it possible to reach the technological limit of lithium-ion batteries. In particular, the theoretical limit of the energy density has almost been reached for the graphite anode material, LiC₆ (372 mA h g⁻¹), through the development of highly crystalline graphite materials and the optimization of the electrolyte composition [1].

Alloy-based anode materials have been extensively studied as alternatives to graphite, due to their higher energy density. However, the major drawback of these materials is their poor capacity retention characteristics, since a large volume change occurs

during cycling. Recently, this problem has been significantly improved by several methods, such as the use of an amorphous composite oxide [2], active–inactive composites [3], intermetallic compounds [4], and metal–carbon composites [5,6].

Mg-based intermetallic compounds with an antifluorite structure, Mg₂X (X = Si, Ge, Sn, Pb), have attracted a certain amount of attention, due to their numerous advantages, such as their high capacity and favorable voltage plateau [7–13]. Previously, our research group studied the reaction mechanism of Mg₂Si [8], Mg₂Sn [9], and Mg–Ni alloys [14] with Li, and found that Mg exhibits a very low voltage plateau (below 100 mV versus Li/Li⁺) during its reaction with Li under galvanostatic conditions at ambient temperature. Although the electrochemical alloying/dealloying of Mg with lithium has been studied at high temperature or using Li–Mg alloys, few studies had been done on the Mg–Li alloying reaction at ambient temperature [15–18]. The alloying reaction between Li and Mg does not occur at a constant current of more than 10 mA g⁻¹, indicating the poor rate capability of pure Mg, probably due to the presence of a native oxide film or solid electrolyte interface (SEI) on its surface [14].

In this study, Mg–C composite was prepared using the high energy mechanical milling (HEMM) technique and its

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electrochemical behavior was investigated, in order to examine its potential as an alternative anode material.

2. Experimental

The active materials were prepared by the following process: Mg (99.9%, 100 mesh, Kojundo Chemical) and carbon black (Super P) powders were used as precursors for HEMM. The precursor powders with various ratios were put into a hardened steel vial with hardened steel balls at a ball-to-powder ratio of 20:1 by weight. The vial was assembled in an Ar-filled glove box, and installed on SPEX-8000 vibratory mill. Each sample was characterized by X-ray diffraction (XRD, MacScience MXP18A-SRA)

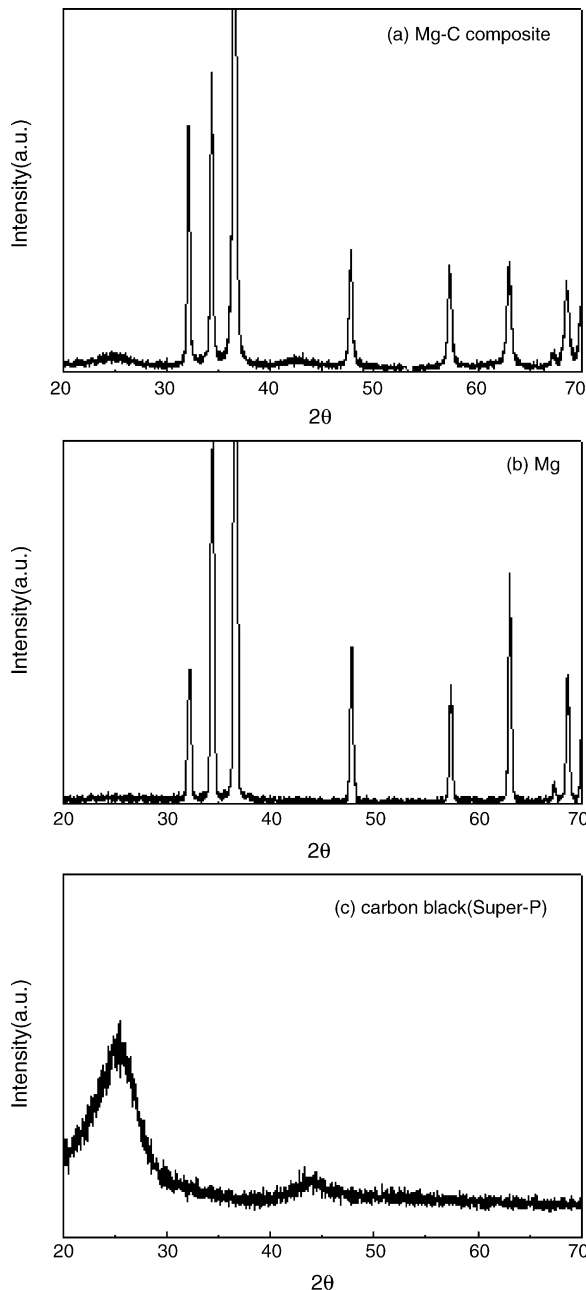


Fig. 1. XRD patterns of: (a) synthesized Mg–C composite; (b) Mg and (c) amorphous carbon black (Super-P).

and Auger electron spectroscopy (AES, Perkin-Elmer, Model 660).

The test electrodes consisted of the powdered active material, carbon black (Super P), as a conducting agent and polyvinylidene fluoride (PVDF) dissolved in *N*-methyl pyrrolidinone (NMP) as a binder, with a mass ratio of 70:15:15, respectively. Each component was well mixed to form a homogeneous slurry, which was coated onto a copper foil, followed by pressing and drying at 120 °C for 4 h under vacuum.

A lab-made coin type electrochemical cell was used with lithium foil as the counter and reference electrodes and 1 M LiPF₆ in a mixed solvent of ethylene carbonate and diethylene carbonate (EC:DEC, 1:1 by volume, Cheil Industries Ltd.) as the electrolyte. The cell was assembled and all electrochemical tests were carried out in an Ar-filled glove box. The charge (Li insertion)/discharge (Li removal) experiments were performed galvanostatically within a voltage window of 0.0–2.0 V (versus Li/Li⁺) at various current rates (5, 30, 50 and 100 mA g⁻¹).

3. Results and discussion

Preliminary studies showed that the optimum composition of Mg to C was 80 to 20 by weight percent. Fig. 1 shows the XRD patterns of the Mg–C (80:20, by weight) composite, Mg,

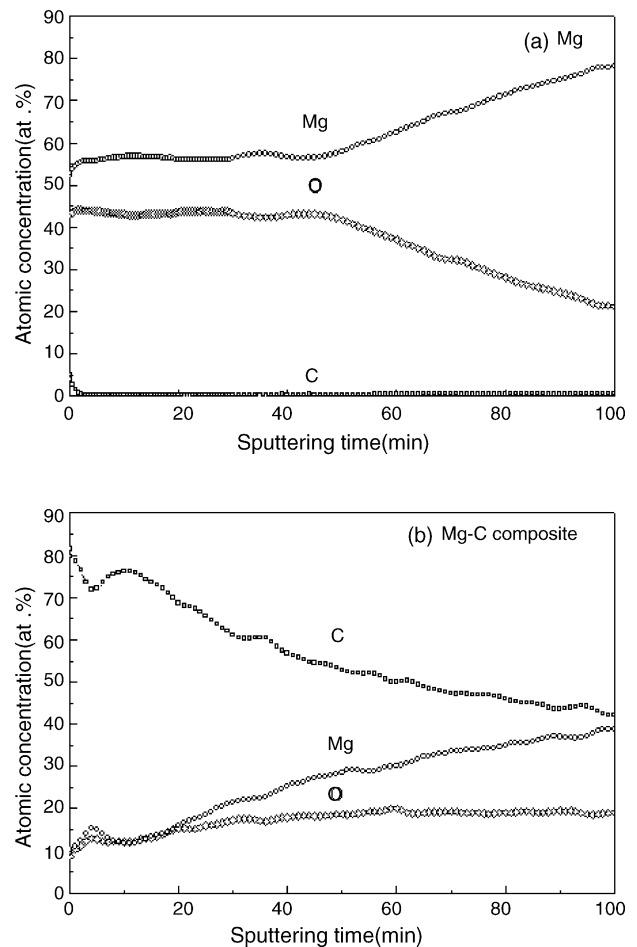


Fig. 2. Concentration/depth profile of: (a) Mg particle and (b) Mg–C composite particle.

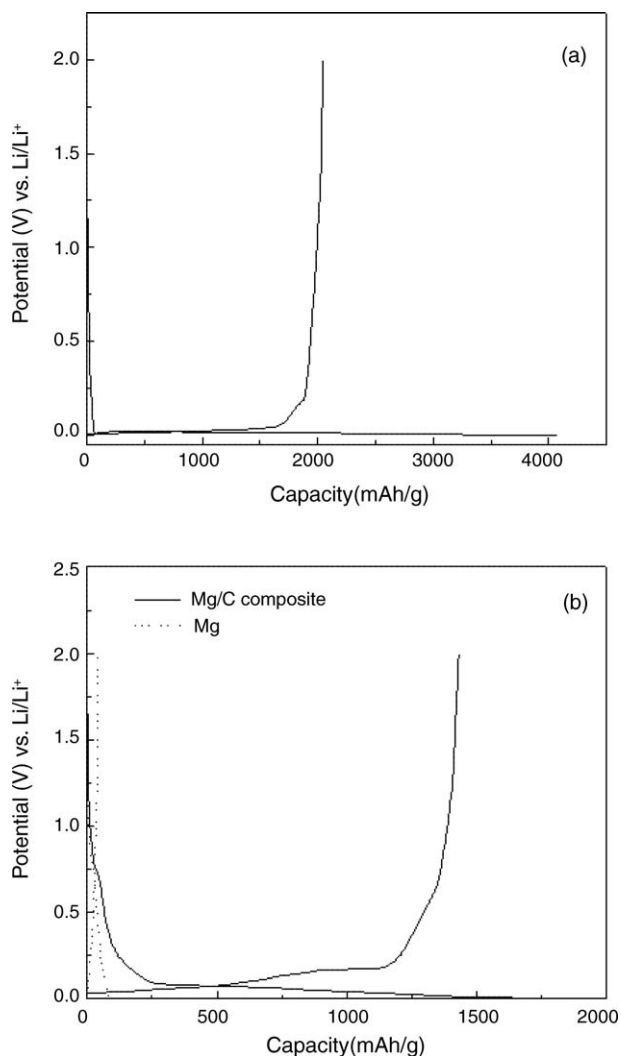


Fig. 3. Voltage profiles of: (a) Mg electrode at a constant current of 5 mA g⁻¹ and (b) Mg-C composite electrode at a constant current of 30 mA g⁻¹ for the first cycle.

and carbon black (Super P). The two broad peaks in the Mg-C composite (Fig. 1a) correspond to carbon and the other sharp peaks are attributed to Mg, while no magnesium carbides such as Mg₂C₃ and MgC₂ were detected.

AES analyses (spot size: 10–100 nm) were performed to determine the compositions of the surfaces of the Mg and Mg-C composite, and the results are shown in Fig. 2. It is well known that the surface of Mg is covered with native magnesium oxide, and its presence can be identified in Fig. 2a. As the penetration depth increases, Mg becomes the major component. However, Fig. 2b shows that the surface of the Mg-C composite is predominantly composed of carbon, indicating that the high energy mechanical milling of Mg with carbon modified the electrode/electrolyte interface.

Fig. 3a shows the voltage profile of the pure Mg electrode at a constant current of 5 mA g⁻¹ for the first cycle, while Fig. 3b shows those of both the Mg and Mg-C composite electrodes at a constant current of 30 mA g⁻¹. The first charge and discharge capacities of the Mg electrode are 4070 and 2039 mA h g⁻¹,

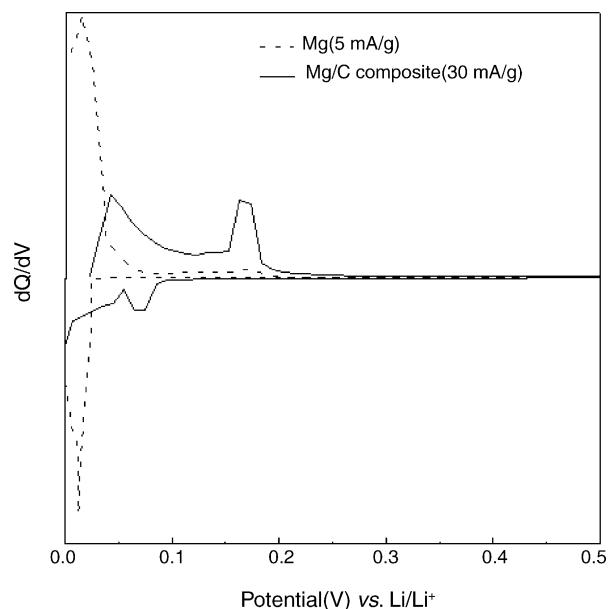


Fig. 4. Differential capacity plots of Mg at a constant current of 5 mA g⁻¹ (dashed line) and Mg-C composite at a constant current of 30 mA g⁻¹ (solid line).

respectively. The voltage profile of Mg displays a very low voltage plateau near 0 V. However, it has been reported that the alloying reaction between Li and Mg does not occur at a constant current of more than 10 mA g⁻¹ [14] and this is also observed in our experiment, as shown in Fig. 3b. The negligible capacity of the Mg electrode at a current of 30 mA g⁻¹ corresponds to the reaction of the conducting agent with Li. The first charge and discharge capacities of the Mg-C composite electrode at the same current of 30 mA g⁻¹ are 1810 and 1433 mA h g⁻¹, respectively. The Coulombic efficiency of the Mg-C composite electrode for the first cycle is about 80%, which reveals that the Mg-C composite significantly enhanced not only the rate capability of Mg, but also the reversibility of the electrochemical reaction of Mg with lithium.

The differential capacity plots (DCP) for the Mg and Mg-C composite electrodes are compared in Fig. 4. The alloying reaction between Mg-C composite and lithium occurs at a higher voltage (70 mV) than that between pure Mg and lithium (12 mV). While the pure Mg was covered with MgO, which acts as a blocking layer to hinder the conduction of electrons and lithium ions, the amorphous carbon on the surface of Mg-C composite is believed to enhance its ionic and electronic conductivity during the alloying reaction with lithium.

The improved reversibility of the electrochemical reaction of Mg with lithium was also observed in the DCP of the Mg-C composite electrode during the dealloying reaction, as shown in Fig. 4. Two peaks can be identified in the differential capacity plots of both Mg and the Mg-C composite during lithium extraction. Considering that Li-Mg alloy has two phases, i.e., the Mg-rich phase (solid solution of Li in Mg) and Li-rich phase (solid solution of Mg in Li) [8], the first peak at around 10–40 mV and the second peak near 170 mV in both the Mg and Mg-C composite electrodes correspond to the phase changes

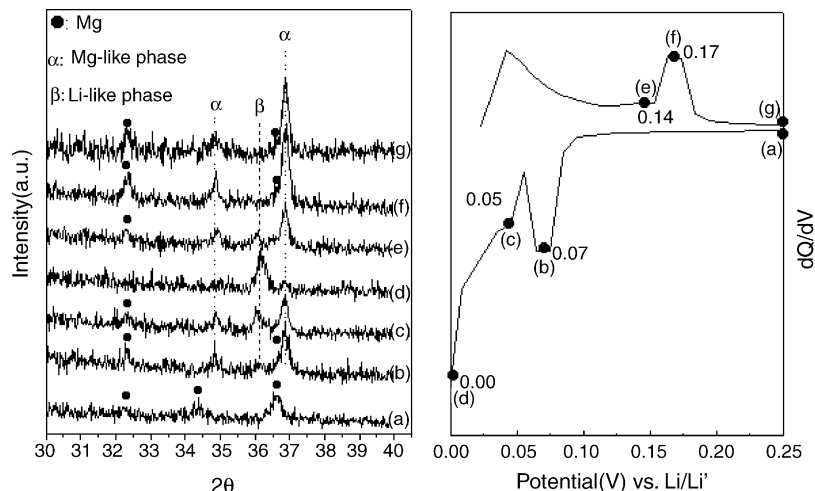


Fig. 5. Ex situ XRD data of the first cycle of the Mg–C composite electrodes: (a) pristine; (b) 0.07 V (Li insertion); (c) 0.05 V (Li insertion); (d) 0.0 V (short-circuited); (e) 0.14 V (Li removal); (f) 0.17 V (Li removal) and (g) 2 V (Li removal).

from the Li-rich phase to the Mg-rich followed by Mg phases, respectively, as confirmed by the ex situ XRD pattern shown in Fig. 5. The XRD patterns of the electrode obtained during the alloying reaction of Mg with lithium show the formation of the Mg-rich phase (Fig. 5b), followed by the formation of the Li-rich phase (Fig. 5c). In the fully lithiated state (Fig. 5d), only the Li rich phase is detected. During the dealloying reaction, the Li-rich phase disappears at 0.17 V (Fig. 5e) and some of the Mg-rich phase still remains, even in the fully delithiated state, which contributes to the irreversible capacity of the Mg–C composite electrode. The ex situ XRD results for the Mg–C composite electrode combined with the differential capacity plot clearly exhibit the sequential phase changes during the alloying/dealloying reaction of Mg with lithium and the irreversible behavior of the Mg-rich phase during cycling.

Fig. 6 compares the cycle performances of the Mg electrode (constant current: 5 mA g^{-1}) and Mg–C composite electrode (constant currents: 30, 50, and 100 mA g^{-1}). The pure Mg electrode shows very poor cyclability within four cycles. The drastic capacity decrease of the Mg electrode is caused by the large volume change associated with the pulverization of the active material and its electrical isolation from the current collector. The capacity retention of the Mg–C composite electrode is better than that of the pure Mg electrode. The carbon on the surface of the Mg–C composite is believed to maintain the electrical conducting network within the electrode even during the dealloying reaction, which ensures the enhancement of the electrochemical reversibility of the Mg–C composite electrode.

4. Conclusions

The Mg–C composite electrode prepared by HEMM showed better rate capability and cyclability than the Mg electrode. The differential capacity plot and ex situ XRD results for the Mg–C composite electrode showed the phase changes during the electrochemical Li–Mg alloying/dealloying reaction. The improvement of the rate capability and capacity retention of the Mg–C composite electrode was attributed to the presence of carbon on the surface of the Mg–C composite, which enhances both the conduction of the electrons and lithium ions during the alloying/dealloying reaction and the reversibility of the electrochemical reaction of Mg with lithium.

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References

- [1] N. Tamura, R. Ohshita, M. Fujimoto, M. Kamino, S. Fujitani, J. Electrochem. Soc. 150 (2003) A679.

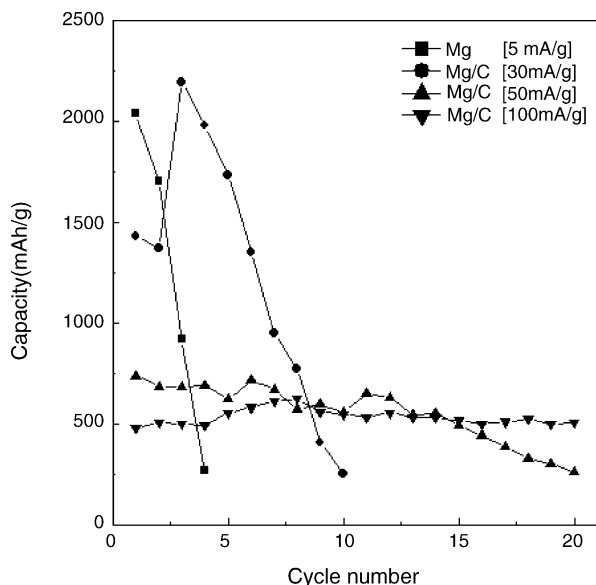


Fig. 6. Discharge capacity vs. cycle numbers of Mg and Mg–C composite electrode.

- [2] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* 276 (1996) 1395.
- [3] O. Mao, B.L. Turner, D.W. McClure, Courtney Ian A., L.J. Krause, J.R. Dahn, *Electrochem. Solid-State Lett.* 2 (1999) 3.
- [4] K.D. Kepler, J.T. Vaughey, M. Thackeray, *Electrochem. Solid-State Lett.* 2 (1999) 307.
- [5] M. Yoshio, H. Wang, K. Fukuda, T. Umeno, N. Dimov, Z. Ogumi, *J. Electrochem. Soc.* 149 (2002) A1598.
- [6] Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, *Electrochem. Solid-State Lett.* 7 (2004) A369.
- [7] H. Sakaguchi, H. Honda, T. Esaka, *J. Power Sources* 81–82 (1999) 229.
- [8] H. Kim, J. Choi, H.-J. Sohn, T. Kang, *J. Electrochem. Soc.* 146 (1999) 4401.
- [9] H. Kim, Y.-J. Kim, D.G. Kim, H.-J. Sohn, T. Kang, *Solid State Ionics* 144 (2001) 41.
- [10] G.A. Roberts, E.J. Cairns, J.A. Reimer, *J. Electrochem. Soc.* 150 (2003) A912.
- [11] S.-W. Song, K.A. Striebel, R.P. Reade, G.A. Roberts, E.J. Cairns, *J. Electrochem. Soc.* 150 (2003) A121.
- [12] G.A. Roberts, E.J. Cairns, J.A. Reimer, *J. Electrochem. Soc.* 151 (2004) A493.
- [13] D. Larcher, A.S. Prakash, J. Saint, M. Morcrette, J.-M. Tarascon, *Chem. Mater.* 16 (2004) 5502.
- [14] H. Kim, B. Park, H.-J. Sohn, T. Kang, *J. Power Sources* 90 (2000) 59.
- [15] A.N. Dey, *J. Electrochem. Soc.* 118 (1971) 1547.
- [16] Y. Iwadate, M. Lassouani, F. Lantelme, M. Chemia, *J. Appl. Electrochem.* 17 (1987) 385.
- [17] A. Anani, R. Huggins, *J. Power Sources* 38 (1992) 363.
- [18] Z. Shi, M. Liu, D. Naik, J.L. Gole, *J. Power Sources* 92 (2001) 70.