Properties of Magnesium Electrode Covered with Magnesium Chloride-Modified Graphene Oxide

Minato EGASHIRA* and Kaori HIRATSUKA

College of Bioscience and Engineering, Nihon University, Kameino, Fujisawa, Kanagawa 252-0880, Japan

* Corresponding author: egashira.minato@nihon-u.ac.jp

ABSTRACT

For the modification of reversibility of magnesium deposition–dissolution in non-aqueous glyme-based electrolytes, the surface of a magnesium metal or magnesium alloy AZ31 was covered by graphene oxide modified using Grignard reagent. After modification, the magnesium chloride moieties appeared to connect with oxygen-containing functional groups of graphene oxide. The magnesium electrode covered with MgCl-modified graphene oxide exhibited a reversible redox reaction assigned to the deposition–dissolution of magnesium from the substance without overpotential in a conventional magnesium salt–glyme solution. The MgCl-modified graphene oxide-covered magnesium alloy electrode was compatible with two-electrode test cells with Mo$_6$S$_8$ positive electrode.

Keywords: Graphene Oxide, Magnesium Batteries, Magnesium Chloride, Magnesium Negative Electrode

1. Introduction

Batteries having a negative magnesium electrode have been attractive as candidates for next-generation power sources of mobile electronics and electric vehicles because of their potentially high energy density and abundant resources. However, at present, trials for practical magnesium batteries have been adversely affected by the high overpotential and low reversibility of magnesium electrode processes. Electrolyte solutions of several kinds have delivered reversible magnesium deposition–dissolution reactions with low overpotential. Among previously proposed candidates, chloride-containing electrolytes such as Grignard reagents without or with Lewis acid addition, MgCl$_2$ with AlCl$_3$, and Mg(TFSI)$_2$ with MgCl$_2$ (TFSI: bis(trifluoromethane sulfonyl)imide) have attracted wide attention and have been investigated intensively during the last few decades. In these chloride-containing electrolytes, various active species for reversible magnesium deposition have been included in an artificial SEI layer of magnesium metal or magnesium alloy AZ31 covered with MgCl-modified graphene oxide (GO–MgCl) was dispersed on the Mg surface. The GO-modified graphene oxide-covered magnesium alloy electrode was compatible with two-electrode test cells with Mo$_6$S$_8$ positive electrode. Alternatively, in some cases, magnesium alloy AZ31 foil (0.085 mm thickness; Fuji Industry Co., Ltd., Japan) was substituted oxidized; Aldrich) of ca. 50 mg was dispersed in ca. 3 cm$^3$ of tetrahydrofuran (THF) solution (Grignard reagent; Kanto Pure Chemical Co., Ltd., Japan). The suspension was stored longer than 2 h so that the attack coordination. These surface layers have provided a certain effect. Nevertheless, changes in the reactivity of magnesium at the negative electrode interface appear to be rather mild; considerable overpotential between magnesium deposition–dissolution has been observed in spite of such modifications.

For this study, an alternative approach is used by which a surface structure containing active magnesium chloride species enhancing reversible magnesium electrode processes has been provided on magnesium. Magnesium chloride moieties might have been anchored by oxygen-containing functional groups in graphene oxides (GOs). The modified GOs have formed a layer on the magnesium surface. Therefore, the coverage of this functionalized GO on the magnesium surface is expected to provide similar chemical status to that of alcoxy-MgCl containing electrolytes. The magnesium electrode with this functionalized GOs shows a reversible magnesium electrode reaction without overpotential, even in conventional Mg(TFSI)$_2$/glyme solution.

2. Experimental

Commercially available graphene oxide (GO, 15–20 sheets, 4–10% oxidized; Aldrich) of ca. 50 mg was dispersed in ca. 3 cm$^3$ of 1 mol dm$^{-3}$ methylmagnesium chloride (MeMgCl)/tetrahydrofuran (THF) solution (Grignard reagent; Kanto Pure Chemical Co., Ltd., Japan). The suspension was stored longer than 2 h so that the attack MgMgCl to oxygen-containing moieties at edges of GO was expected to proceed sufficiently. Several cubic centimeters of this suspension were dropped on a preliminarily polished magnesium plate (99.9%, 0.10 mm thickness; The Nilaco Corp., Japan). Alternatively, in some cases, magnesium alloy AZ31 foil (0.085 mm thickness; Fuji Industry Co., Ltd., Japan) was substituted to magnesium metal. The magnesium plate was then washed several times with THF to remove excess MeMgCl, followed by vacuum drying after each washing. These processes were conducted in an Ar-filled glove box and an attached entry box for vacuum drying. After these processes, the GO modified with MeMgCl (hereinafter denoted as GO-MgCl) was dispersed on the Mg surface. The expected loading amount of GO-MgCl was ca. 2 mg cm$^{-2}$ of the Mg surface, although a certain amount of GO-MgCl must be eluted off.
The existence of chlorine-containing species on the GO-MgCl/Mg was confirmed using X-ray photoelectron spectroscopy (XPS; K-alpha; Thermo Scientific) with an Al Kα monochromatic source. The binding energy scale was calibrated with respect to the C 1s signal at 284.8 eV. The XPS measurements were conducted for the GO-MgCl/Mg and pristine magnesium plate. The XPS spectrometer does not include any transfer vessel attachments. Therefore, the samples were transferred from a hermetically sealed container to sample holders as rapidly as possible.

The electrochemical properties of the GO-MgCl/Mg were evaluated using cyclic voltammetry (CV). The cell for the CV measurement was a commercially available one (011951; BAS Inc., Japan). The GO-MgCl/Mg prepared using various conditions was used as a working electrode, magnesium was used as a counter electrode. Also, a Ag/Ag⁺, a silver wire in AgNO₃/acetonitrile (BAS Inc., Japan) was used as a reference electrode. A solution of Mg(TFSI)₂ (Battery-grade; Kishida Chemical Co., Ltd., Japan) of 1.5 mol dm⁻³ in triglyme (Battery-grade; Kanto Pure Chemical Co., Ltd., Japan) or 1.2 mol dm⁻³ in diglyme (Battery-grade; Kanto Pure Chemical Co., Ltd., Japan) was used as the electrolyte, unless otherwise denoted. Preparation of the electrolyte, cell components and assembly of the cell with a glass-filter separator (GF/A; Whatman) were all conducted in an Ar-filled glove box. The assembled cell was stored in a sealed container with external connections. The container was removed from the glove box. The temperature of the whole container was controlled using a temperature chamber (SU-221; Tabai Espec. Corp., Japan). The CV measurements were taken using a potentiostat (1286; Solartron Analytical), under the scan rate of 5 mV s⁻¹ between –3.5 (or on some cases –4.0) and 1.0 V at 298 K or 333 K. The properties of GO-MgCl/Mg as a negative electrode of magnesium secondary batteries were also evaluated using test cell studies. The test cell included the GO-MgCl/Mg negative electrode, Chevrel phase molybdenum sulfide Mo₆S₈ positive electrode, and 1.2 mol dm⁻³ Mg(TFSI)₂/diglyme electrolyte. Mo₆S₈ was laboratory-made, kindly provided by Prof. S. Yagi, the University of Tokyo, Japan. Mo₆S₈ powder was mixed with poly(vinylidene difluoride)/PVdF binder and acetylene black conductive agent in 1-methyl-2-pyrrolidinone solvent, and was spread on current-collector metal film. The test cell body was a commercially available one (HS-1; Hohsen Corp., Japan). Both the magnesium plate and positive electrode film were cut into circular form of 14 mm diameter. The GO-MgCl/Mg negative electrode was prepared using the procedure described above with a circular-cut magnesium plate. The cell was assembled with both electrodes, ca. 1 cm² of electrolyte, and a glass-filter separator (GF/A; Whatman) in an Ar-filled glove box. The assembled cell was taken out and connected with a charge–discharge power supply (HJ1020m; Hokuto Denko Corp., Japan). The charge–discharge condition was the C/200 current rate for positive electrode active material. The cut-off voltages were 1.4 V for charging and 0 V for discharging. During the charge–discharge test, the cell temperature was not controlled (ca. 298 K).

3. Results and Discussion

Figure 1 presents micrographs of (a) the magnesium plate and (b) the GO-MgCl/Mg surface. The traces by mechanical polish are observed clearly on the magnesium plate. The surface of the GO-MgCl/Mg differs markedly from that of the original magnesium, indicating coverage by particles of functionalized graphene oxides. Electrolyte can immerse into the interparticular spaces and create interface between magnesium electrode.

The XPS spectra of magnesium and the GO-MgCl/Mg at the limited binding energy region for carbon, magnesium and chlorine elements are shown in Fig. 2. The addition of chlorine-containing species on the GO-MgCl/Mg is indicated by marked peaks at 198 and 200 eV, assigned to 2p₃/2 and 2p₁/2 for chlorine. From the peak area, the atomic ratio of chlorine on the surface of the GO-MgCl/Mg is ca. 11–12 %. Although it is difficult to evaluate bonding of the chlorine by these peaks, these chlorine atoms remain on the surface after the vacuum environment in the XPS chamber, likely by a strong bonding on the surface. The original magnesium has a one large peak at 285 eV in the C 1s region, assigned to the elemental carbon contaminated in these samples and used for the calibration. For the GO-MgCl/Mg, a shoulder peak is found at 286.5 eV in addition to the 285 eV peak. The chemical shift of this shoulder peak corresponds to the peak for C–C bonding. Consequently, this peak is thought to represent graphene oxide. A small peak around 290 eV, assigned to the carbon in carbonate, is observable only for magnesium, indicating that carbonate species is not exposed in the GO-MgCl/Mg surface. In addition, a peak at Mg 2p region is

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Optical micrographs of the magnesium surface. (a) magnesium (b) GO-MgCl/Mg (c) cross-sectional illustration of GO-MgCl/Mg.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** XPS spectra of magnesium (dotted line) and the GO-MgCl/Mg (solid line) at selected regions. (a) C 1s region (b) Mg 2p region (c) Cl 2p region.
shifted to lower binding energy by the coverage of the GO-MgCl, suggesting that magnesium species exists at reduced states in the GO-MgCl/Mg compared with magnesium. The overall XPS results indicate that the GO-MgCl consists of the graphene framework bound with a significant amount of chlorine. The graphene was modified successfully, as expected.

Cyclic voltammograms of the magnesium plate electrode in 1.5 mol dm$^{-3}$ Mg(TFSI)$_2$/triglyme electrolyte at 298 K and 333 K are shown respectively in Figs. 3(a) and 3(b). The reduction current, assigned to magnesium deposition, is observed at $-2.3$ V vs. Ag/Ag$^+$. The corresponding oxidation, magnesium dissolution, current is observed at 0.2 V vs. Ag/Ag$^+$ at 298 K. The intersections of the potential axis for the reverse scans of both reduction and oxidation currents become closer to each other by 0.1 V, indicating that the nucleation overpotential was added to the onset potential of the reduction at the cathodic scan, and also of oxidation at the anodic scan. Even if the contribution of nucleation overpotentials are neglected, large overpotential of 2.2 V was observed between magnesium deposition–dissolution was observed. The cyclic voltammograms of magnesium plate coated by GO without modification at 298 K and 333 K are shown respectively in Figs. 3(c) and 3(d). The presence of GO, even the modification, on magnesium has a certain effect of decreasing the overpotential of magnesium deposition–dissolution by decreasing the onset potential of magnesium dissolution. However, the effect is insufficient. Still, ca. 1.5 V of the overpotential of magnesium deposition–dissolution remained. Cyclic voltammograms of the GO-MgCl/Mg electrode at the same condition are presented in Figs. 3(e) and 3(f). Even at ambient temperature, this electrode shows reversible magnesium deposition–dissolution currents around $-2.1$ V vs. Ag/Ag$^+$ without overpotential. This behavior is similar to the magnesium deposition–dissolution in a chlorine-containing electrolyte. It is surprising that the reversible magnesium deposition–dissolution was observed not by magnesium–chlorine complexes in the electrolyte but by the magnesium halide on the electrode surface. At around $-1.5$ V at the cathodic scan, irregular oxidation current onset is observed. This current is reproducive, even under different conditions, such as Figs. 3(e) and 3(f). A certain change, such as rearrangement, of the GO-MgCl might activate magnesium dissolution. Generally, Grignard reagent favors a reductive environment. Therefore, -MgCl moiety might be activated by reductive potential. At 333 K, both the oxidation and reduction currents show no peak. They continue to increase with the development of potential from equilibrium. Such current behaviors imply that the magnesium deposition–dissolution do not achieve a diffusion–limited step. Therefore the substance magnesium might participate to the reactions. In other words, the MO-MgCl does not simply provide reactive magnesium as an active species: it activates the substance magnesium. In contrast, some voltammograms, in particular obtained by the operation at 298 K, show a current peak during oxidation process. This peak delivers two kinds of hypotheses on the magnesium dissolution reaction: one is that only magnesium freshly deposited may participate in the dissolution process, the cyclic voltammetry was started from the scanning to the positive direction. The resulted voltammogram at the first and second cycle is shown in Fig. 4. In this graph, contrary to the other ones in this paper, the first cycle voltammogram at the positive potential region is indicated by solid line. The current at the first positive scan is very small even with the GO-MgCl coverage, although the second cycle curve is very similar to the voltammogram obtained from the measurement started from negative scan. This result may suggest that the GO-MgCl/Mg promotes the deposition of fresh magnesium on the magnesium substance and subsequent smooth dissolution–deposition of the initially deposited magnesium, without the activation of the substance magnesium. As another hypothesis, some change on the surface may occur at a certain negative potential which promote smooth magnesium deposition–dissolution. The similar current...
onset observed around $-1.5\,\text{V}$ at negative scan may be the sign of the surface rearrangement.

Cyclic voltammograms of magnesium deposition–dissolution in 1.2 mol dm$^{-3}$ Mg(TFSI)$_2$/diglyme at 298 K is shown in Fig. 5(a). Diglyme solvent appears to be preferable compared with triglyme for this system, from larger current and rather stable cycle behavior. Various glymes are expected to be effective for this purpose. For practical application, magnesium alloy AZ31 might be superior to pure magnesium metal in terms of cost and engineering. Surface modification of AZ31 has also been conducted similarly. The obtained electrode was denoted as GO-MgCl/AZ31. The cyclic voltammogram of magnesium deposition–dissolution of GO-MgCl/AZ31 electrode in Mg(TFSI)$_2$/diglyme electrolyte at 298 K is shown in Fig. 5(b). The electrode behavior of this electrode is intrinsically similar to that of its analogue pure magnesium substance, with reversible magnesium deposition without overpotential, even with coexistence of other components such as aluminum and zinc. The current flow is somewhat greater in this case. Therefore, the GO-MgCl/AZ31 electrode was used for the following test cell studies.

Results indicate that the Mg(TFSI)$_2$/diglyme electrolyte is superior to the Mg(TFSI)$_2$/triglyme for stable magnesium deposition–dissolution. Therefore, using the Mg(TFSI)$_2$/diglyme electrolyte, two-electrode cell of the GO-MgCl/AZ31 negative electrode with Chevrel Mo$_6$S$_8$ positive electrode was assembled. The constant-current charge–discharge curves for the GO-MgCl/AZ31//Mo$_6$S$_8$ cells are shown in Fig. 6. As shown on the horizontal axis, specific capacity mAh g$^{-1}$ is based on the active mass of a positive electrode. At the present stage, the specific capacity of the cell did not achieve sufficient values, mainly because preparation of the positive electrode composite was not yet optimized. However, somewhat smooth charge–discharge reactions were observable. The fluctuation of curves is attributable mainly to the change of temperature, which directly affects the cell temperature when no temperature control is used. The plateau voltage includes information related to the extent of overpotential by the negative electrode resistance in the deviation of plateau voltage between charging and discharging processes. From Fig. 6, the initial points of charging and discharging plateaus are shown to lie respectively at 0.9 V and 0.8 V. The difference between initial voltages of charging and discharging, including magnesium electrode overpotential, is as small as 0.1 V. This small overpotential, even in non-halogen Mg(TFSI)$_2$/diglyme electrolyte, clearly indicates positive effects of the GO-MgCl layer in a test cell setting. For comparison, a stainless steel electrode covered with the GO-MgCl (GO-MgCl/SS) was prepared. A test cell with Mo$_6$S$_8$ positive electrode was assembled. The charge–discharge curve of the GO-MgCl/SS//Mo$_6$S$_8$ cell with Mg(TFSI)$_2$/diglyme electrolyte is also included in Fig. 6. The charge–discharge behavior of this cell differed considerably from that of the analogue with the GO-MgCl/AZ31 negative electrode: the GO-MgCl/SS negative electrode delivers negligible discharge capacity. This difference in charge–discharge behaviors clearly indicates the consumption of not only the freshly deposited magnesium but the magnesium substance as an active species.

The unique redox properties of the surface-coated magnesium electrode might provide information about the role of halogen species and the mechanism of magnesium deposition–dissolution in halogen-containing electrolytes, through intermediate Mg–Cl complex species at the neighborhood of magnesium. Further modification of such solid phase components with magnesium halide moiety and surface analyses is expected to bring progress in these areas. At the present stage, the GO-MgCl particles are not fixed on magnesium surface. Therefore, the coverage was mostly sloughed off when the cell was disassembled after the charge-discharge cycles. Further attempt is necessary to improve the adhesion of the GO-MgCl for the long-term stability of this composite electrode.

4. Conclusion

By the coverage of graphene oxides attaching –MgCl moiety on the magnesium surface, the surface-coated magnesium electrode (GO-MgCl/Mg) has been prepared successfully. The GO-MgCl/Mg electrode shows reversible redox, assigned to magnesium deposition–dissolution, with very small overpotential, even at ambient temperature and in a conventional Mg(TFSI)$_2$/glime electrolyte system. Regarding the electrode process, magnesium from magnesium metal or magnesium alloy substance acts as an active mass. The test cells using the surface-coated magnesium alloy electrode GO-MgCl/AZ31 together with Mo$_6$S$_8$ positive electrode function with only slight deviation between the charging and discharging plateaus, even in Mg(TFSI)$_2$/diglyme electrolyte.
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