Electrochemical $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ Intercalation/de-intercalation into Graphite Electrode as the Positive Electrode Reaction for Mg Secondary Batteries

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ABSTRACT

The electrochemical $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ (TFSA[−]) anion intercalation into graphite was studied, aiming at the use for Mg secondary batteries. In order to achieve both the Mg plating/stripping reaction and anion intercalation, the electrolyte solution consisting of Mg^{2+} /glyme = 1 (mol) with hydrofluoroether (HFE) as the diluent was used. The Raman spectrum indicated that all glyme solvated Mg^{2+} -ion, which led the improvement of anti-oxidation durability up to 4.5 V (vs. Mg^{2+}/Mg). The TFSA[−] anion intercalation took place in the solution with almost 100% of coulombic efficiency. Besides, the charge-discharge test exhibited the discharge plateau over 3.4 V (vs. Mg^{2+}/Mg) with the capacity of ca. 70 mAh g^{−1}. The results indicated the anion intercalation into graphite will be the attractive candidate for Mg secondary batteries.

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Keywords : Mg Secondary Batteries, Anion Intercalation, Solvate Ionic Liquid, Mg Plating

1. Introduction

Lithium-ion batteries (LIBs) are widely used in electric devices such as smart phones, laptop PCs, and electric vehicles. On the other hand, LIBs are faced with their limit of energy densities, high costs, safety problems and therefore, the research and development of post LIBs is paid much attention. Among them, Mg plating/stripping reaction is attractive as the negative electrode reaction due to its relatively low electrode potential of −2.36 V (vs. NHE) and high theoretical capacity of 3839 mAh cm^{−3}. Besides, unlike Li resources, Mg resources are abundant and widely distributed, which leads lower cost. Although the use of metal plating/stripping in secondary batteries is generally difficult due to the localized plating and the following dendrite formation, Ling et al. reported that Mg was preferable to form high dimensional morphology, rather than 1D growth,¹ which implies the use of Mg metal as the negative electrode, i.e., the development of Mg secondary batteries will be realistic.

However, Mg secondary batteries have a lot of problems to be solved. Firstly, the negative electrode reaction, i.e., the plating/stripping of Mg metal is fairly difficult. The fresh Mg surface is highly reactive to cause the reduction of the electrolyte solution and the following surface film formation.² Although the similar surface film formation also takes place for Li metal or negative electrodes in the Li⁺-ion batteries, the surface film, so called solid electrolyte interphase, is Li⁺-ion conductive and electron insulative, so the reversible electrode reaction (Li metal plating/stripping or Li⁺-ion insertion/extraction) is achieved without the continuous electrolyte decomposition. On the other hand, the surface film on the Mg metal is generally insulative and so far, any clear evidence about Mg^{2+} -ion conductive surface film has not been reported.² Therefore, the reported electrolyte solutions for the reversible Mg metal plating/stripping reaction are almost limited to the ethereal based solutions because of their excellent anti-reduction capability.^{3–5} Among them, glyme based solutions dissolving $\text{Mg}(\text{N}(\text{CF}_3\text{SO}_2)_2)_2$ ($\text{Mg}(\text{TFSA})_2$) are widely studied due to their relatively high ionic conductivity and anti-oxidation capability.^{6–12} The coordination structure of $\text{Mg}(\text{TFSA})_2$ /glyme solutions has been studied and found that Mg^{2+} -

ion was solvated by glyme molecules to form 1 : 2 complex.¹³ Kitada et al. reported that the complex was maintained in the glyme/ionic liquid co-solvent systems and the solvating structure realized the Mg plating reaction in the ionic liquid based electrolytes.¹⁴ We confirmed the importance of the solvation between Mg^{2+} -ion and ethereal solvent by using crown ethers and achieved the Mg plating in the ionic liquid electrolytes by forming 1 : 1 complex of Mg^{2+} -ion and 18-crown-6.⁹

Secondary, the positive electrode materials are also faced with the serious problems. Like LIBs, the positive electrode reaction is also assumed to use the insertion/extraction of Mg^{2+} -ion in the host materials. However, the electrochemical behavior of Mg^{2+} -ion system is much inferior to that of Li⁺-ion. Mg^{2+} -ion strongly interacts with the solvent species or host lattice, so the charge transfer at the electrode/electrolyte interface and the diffusion in the electrode materials need large overpotential.^{15,16} In fact, spinel materials, such as MgCo_2O_4 and MgMn_2O_4 , are paid much attention as the 3 V class electrodes, but their charge and discharge reaction often require the overpotential of as large as 1 V.^{17,18} The large overpotential lowers the operating voltage to 2 V and also causes the oxidation decomposition of the ethereal solutions during the charge process.

The serious issues concerning positive electrode reaction mentioned above motivated us to use alternative candidate as the positive electrode reactions. Anion species, such as PF_6^- , BF_4^- and TFSA[−] have been reported to intercalate into the graphite electrode at as high as over 4.5 V (vs. Li⁺/Li), i.e., 3.8 V (vs. Mg^{2+}/Mg) without any clear overpotential and therefore, anion intercalation reaction is expected to use in dual carbon batteries or hybrid capacitors.^{19–24} In the present study, we focus on the TFSA[−] intercalation into the graphite electrode as the positive electrode reaction toward Mg metal negative electrode. The batteries are expected to free from the large overpotential of the positive electrode reaction and to show 3 V of operating voltage. However, the glyme based solutions decompose around at 3.5 V (vs. Mg^{2+}/Mg), which takes place prior to the TFSA[−] intercalation, so the improvement of the anti-oxidation capability must be achieved. In order to give the glyme based solutions enough anti-oxidation

stability, we use the concentrated solution consisting of $\text{Mg}(\text{TFSA})_2$: glyme = 1 : 1 (mol). Recently, some groups have reported that the electrochemical window of the solvent species have been improved by excluding free solvents and these concentrated solutions are widely studied as new class of electrolytes.^{25–27} However, these super concentrated solutions are not suitable for the batteries' electrolyte solutions due to their high viscosity and high cost. Especially, $\text{Mg}(\text{TFSA})_2$ is much expensive than LiTFSA , so the concentrated solution using $\text{Mg}(\text{TFSA})_2$ is not realistic. Recently, Watanabe et al. reported the solvation structure between Li^+ -ion and glyme solvent was maintained even when the 1 : 1 (mol) solution was diluted by some kinds of hydrofluoroether.²⁸ From the reports above, we led to the idea that the electrolyte solutions for Mg secondary batteries with anion intercalation reaction would be realized with lower cost.

In the present paper, we studied the TFSA^- intercalation/de-intercalation into the graphite electrode in the $\text{Mg}(\text{TFSA})_2$: glyme = 1 : 1 (mol) solutions with hydrofluoroether as the diluent. We found the TFSA^- intercalation reaction took place with high coulombic efficiency in even in the glyme based solutions and also confirmed the Mg plating was achieved in the solution. The results will indicate the anion intercalation into graphite is an attractive candidate as the positive electrode reaction toward Mg metal negative electrode.

2. Experimental

Electrochemical behavior of the graphite electrode was studied by a beaker-type three electrode cell. Highly oriented pyrolytic graphite (HOPG (HYZ grade), ca. 1.5 mm × 1.5 mm × 0.25 mm) bound with Pt wire was used as the model electrode, in which, no binders nor conductive additives were contained, so we could observe the pure graphite electrode behavior. Counter electrode was Mg ribbon (nilaco), which was polished in the Ar-filled glove box before use. Reference electrode was Ag wire in 0.01 mol dm⁻³ AgNO_3 + 0.1 mol dm⁻³ $\text{Mg}(\text{TFSA})_2$ /triglyme, which was separated from the electrolyte solution by the porous glass. The Mg plating/stripping reaction in the Grignard reagent based solution was confirmed at about -2.5 V with the reference electrode above, so unless otherwise mentioned, all electrode potential were referred to Mg^{2+}/Mg . Electrolyte solution consisted of $\text{Mg}(\text{TFSA})_2$ (Kishida chemicals) dissolved in diglyme (Aldrich) and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (HFE, Tokyo Kasei). In the solutions, the molar ratio of Mg^{2+} /diglyme was kept to be 1 and HFE was used as the diluent. As comparison, 0.5 mol dm⁻³ $\text{Mg}(\text{TFSA})_2$ /diglyme was also prepared. All electrolyte solutions were dried by molecular sieves and the residual water was confirmed to be less than 50 ppm by Karl-Fischer titration technique. The coordination condition of Mg^{2+} -ion in the solutions were investigated by Raman spectroscopy (Jasco NRS-3200) with 532 nm laser radiation.

The anti-oxidation stability of the solutions against Pt working electrode was studied by linear sweep voltammetry. The electrochemical TFSA^- intercalation/de-intercalation into the graphite electrode was investigated by cyclic voltammetry with Solartron 1470E. X-ray diffraction (XRD) was conducted to confirm the graphite intercalated compound (GIC) formation (Rigaku Rint UltimaIV). As for charge-discharge test, the composite electrode consisted of graphite (SGP-5, SEC carbon) : Ketjenblack : PVdF = 90 : 3 : 7 (wt%) on Al current collector was used. The beaker type cell consisted of the sandwich structure of the composite electrode/glass filter/Mg soaked in the electrolyte solution and the reference electrode mentioned above was used. The specific capacity was assumed as 100 mA h g⁻¹, which was experimentally reported by several groups,^{22,29} and the current density was set to be 20 mA g⁻¹ (1/5 C rate) (HOKUTO SD8). Cut off potential was set at 4.5 V (vs.

Mg^{2+}/Mg) and 2.5 V (vs. Mg^{2+}/Mg) for three electrode measurements. Two electrode measurement was also conducted between 0–4.8 V. All electrochemical cells were fabricated in the Ar filled glove box (the dew point was below 193 K) and electrochemical measurements were conducted under Ar atmosphere at 333 K due to the high viscosity of the solutions.

3. Results and Discussion

3.1 Solvation structure in the HFE diluted solutions

In order to improve the anti-oxidation capability, all glyme molecules must solvate Mg^{2+} -ion. Figure 1(a) shows the Raman spectra for the solutions at the frequency range of 780–900 cm⁻¹, which contains C-O-C stretching mode and CH₂ rocking mode of glyme molecules. They are known to be sensitive to the solvation structure.³⁰ In order to exclude the effect of HFE, the subtracted spectra are also shown in Fig. 1(b). In 0.5 mol dm⁻³ $\text{Mg}(\text{TFSA})_2$ /diglyme solution, the peak at 805 cm⁻¹ and 889 cm⁻¹ are observed and the peaks correspond to the free and bounded glyme, respectively. On the other hand, in $\text{Mg}(\text{TFSA})_2$: diglyme : HFE = 1 : 1 : 4 (mol) and 1 : 1 : 3 (mol) solutions, the peak at 805 cm⁻¹ almost disappears. The result will mean that the free glyme no longer exists and all glyme molecules bind Mg^{2+} -ion. This is also supported by the peak at 879 cm⁻¹, which corresponds to the bounded glyme. The peak difference from 0.5 mol dm⁻³ solution case (889 cm⁻¹) will be caused by the solvation structure. In the 1 : 1 : 4 (mol) and 1 : 1 : 3 (mol) solutions, the same amount of Mg^{2+} -ion and diglyme molecules exists, so the Mg^{2+} -ion will be solvated to form 1 : 1 complex. On the other hand, in 0.5 mol dm⁻³ solution, the amount of glyme molecules is much larger than that of Mg^{2+} -ion (Mg^{2+} /diglyme = 1/14 (mol)) and in the case, Mg^{2+} -ion is reported to form 1 : 2 complex.¹³ Unfortunately, however, the solubility of $\text{Mg}(\text{TFSA})_2$ to diglyme was not high enough to prepare 1 : 2 (mol) solution, we could not compare the Raman spectra. We speculate the reason why 1 : 1 complex was achieved in the HFE diluted solution is that HFE also solvates Mg^{2+} -ion, although $\text{Mg}(\text{TFSA})_2$ hardly dissolve in HFE. Anyway, we can conclude the solvation between Mg^{2+} -ion and diglyme was maintained in the diluted solutions by HFE, as reported in Li-salt case.²⁸

The coordination condition of TFSA^- in the solutions were also discussed. Figure 2(c) shows the Raman spectra for the solutions at the frequency range of 700–800 cm⁻¹. The band at around 740–750 cm⁻¹ corresponds to the C-F symmetric deformation mode and it is helpful to know the interaction of TFSA^- anion.³¹ 0.5 mol dm⁻³ solution shows a peak at 742 cm⁻¹, which means that TFSA^- anion exists as free anion. On the other hand, the Raman bands for the 1 : 1 : 3 (mol) and 1 : 1 : 4 (mol) solutions shift to the higher wavenumber and split into two peaks. According to the theoretical calculation, the lower and higher peak are attributed to the solvent shared ion pair and the contact ion pair, respectively.²⁸ The results indicate that a part of TFSA^- anion interacts with Mg^{2+} -ion to form the contact ion pair. The correlation between the coordination structure and the intercalation reaction is discussed later.

3.2 The effect of HFE on the electrochemical Mg plating/stripping reaction

Since the Mg plating reaction is often inhibited even by a slight impurity, we firstly studied whether the Mg plating took place or not in the HFE contained solution. Figure 2(a) shows the cyclic voltammogram (CV) of Pt electrode in the $\text{Mg}(\text{TFSA})_2$: diglyme : HFE = 1 : 1 : 3 (mol) or in the 1 : 1 : 4 (mol) solution. In the 1 : 1 : 3 (mol) solution, a reduction current is observed from -0.5 V (vs. Mg^{2+}/Mg), indicating the Mg plating reaction took place even in the HFE contained solution. Figure 3(a) shows the XRD pattern of the deposits after potential holding at -1.5 V (vs. Mg^{2+}/Mg). From the typical three peaks of Mg metal, we can conclude the Mg

Figure 1. Raman spectra for (a) $\text{Mg}(\text{TFSA})_2$: diglyme based solutions at the range of 900 cm^{-1} – 780 cm^{-1} . (b) HFE-subtracted spectra of (a) and (c) at the range of 800 cm^{-1} – 780 cm^{-1} . Molar ratio in the figure denotes $\text{Mg}(\text{TFSA})_2$: diglyme : HFE.

plating was achieved even in the HFE contained solution. On the other hand, any clear current is not observed in the 1 : 1 : 4 (mol) solution. We also confirmed the Mg plating took place in the 1 : 1 : 1 (mol) and 1 : 1 : 2 (mol) solutions, while any clear reduction current was not observed in the 1 : 1 : 6 (mol) solution, as shown in Fig. SI 1. The results will imply there is some threshold of HFE concentration for the Mg plating reaction. Besides, the oxidation current corresponding to the Mg stripping is hardly seen in the 1 : 1 : 3 (mol) solution, although the $\text{Mg}(\text{TFSA})_2$ /glyme based solutions generally show the poor reversibility and large over-potential for the Mg stripping, as shown in Fig. 2(d). In order to elucidate the poor Mg stripping reaction, the electrochemical behavior of Mg substrate in the 1 : 1 : 3 (mol) solution was also investigated. As shown in Fig. 2(b), in the case of only the anodic sweep was conducted, the oxidation current does not disappear. So the stability of the 1 : 1 : 3 (mol) solution against Mg metal seems to be comparable with that of the $\text{Mg}(\text{TFSA})_2$ /diglyme solution. On the other hand, in the case of both anodic and cathodic scan was conducted, the oxidation current disappears after the cathodic scan, as shown in Fig. 2(c). The results will mean that HFE used in the study is essentially stable against Mg metal, but it seemed to be reduced by cathodic sweep below 0 V (vs. Mg^{2+}/Mg) for the Mg

plating reaction. In fact, the decomposition of HFE is also indicated by the scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX). Figure 3(b) shows the SEM image of the plated Mg metal in the $\text{Mg}(\text{TFSA})_2$: diglyme : HFE = 1 : 1 : 3 (mol) solution obtained by the potential holding at -1.5 V (vs. Mg^{2+}/Mg). Note that any positive scan or potential holding was not conducted, so the sample morphology or EDX analysis reflects just the Mg plating behavior. Generally, the plated Mg tends to show the particulate morphology in the glyme based solutions, as shown in Fig. SI 2. Although the deposit obtained in the HFE contained solution also shows the similar morphology, some characteristic pits are found on the plated Mg surface. The cause of the pit formation is not clear, but we speculate this will be formed by the gas generation during the electrochemical plating or the vacuum dry for SEM observation. In addition, the EDX analysis reveals the relatively high concentration of F is contained in the deposits (N : S : F : Mg = 10 : 0.5 : 22 : 100 (atm %)). From the results, the Mg plating will contain the decomposed products a lot, and this will cause the poor reversibility. Besides, the reason why the Mg plating did not take place in the 1 : 1 : 4 (mol) solution will also be the HFE decomposition. The concentration of HFE in the 1 : 1 : 4 (mol) solution is much higher than that in the 1 : 1 : 3 (mol) solution, so the

Figure 2. (a) Cyclic voltammograms of Pt in $\text{Mg}(\text{TFSA})_2$: diglyme : HFE = 1 : 1 : 3 or 1 : 1 : 4 solutions. Scan rate was set at 5 mV sec^{-1} . CVs of Mg electrode in $\text{Mg}(\text{TFSA})_2$: diglyme : HFE = 1 : 1 : 3 solution for (b) anodic scan only and (c) both cathodic/anodic scan. (d) CV of Mg electrode in 0.5 mol dm^{-3} $\text{Mg}(\text{TFSA})_2$ /diglyme.

decomposition of HFE will preferentially occur. From the results and discussion above, we conclude that the Mg plating reaction can be achieved even in the HFE contained solution, but the optimization of HFE will be necessary. However, we focus on the anion intercalation reaction in the present study, so we used the 1 : 1 : 3 (mol) solution in the following discussion.

3.3 TFSA^- anion intercalation reaction

Figure 4 shows the comparison of the anti-oxidation capability against Pt electrode. In 0.5 mol dm^{-3} $\text{Mg}(\text{TFSA})_2$ /diglyme, the oxidation current appears from ca. 3.5 V (vs. Mg^{2+}/Mg), which corresponds to the oxidative decomposition of glyme solvents. On the other hand, the oxidation durability of the 1 : 1 : 3 (mol) solution is improved up to 4.5 V (vs. Mg^{2+}/Mg). As mentioned above, the Raman spectrum for the 1 : 1 : 3 (mol) solution shows that all diglyme molecules solvate Mg^{2+} -ion and which will lead to the high anti-oxidation capability. Therefore, we confirmed that HFE played as the diluent, and Mg^{2+} -ion and diglyme behaved as the “solvate ionic liquid” even in the diluted solution.

The intercalation/de-intercalation behavior of TFSA^- anion toward HOPG was compared in Fig. 5(a). Although the redox current appears in both solutions, the intensity in the 1 : 1 : 3 (mol) solution is much smaller due to its high viscosity. The high viscosity will also cause the lower potential shift of the reduction peak. Note that in the 0.5 mol dm^{-3} $\text{Mg}(\text{TFSA})_2$ /diglyme, the oxidation current is much larger than the corresponding reduction current, which will indicate the unwanted side reaction, i.e., the decomposition of diglyme takes place. In fact, the coulombic efficiency in the 0.5 mol dm^{-3} $\text{Mg}(\text{TFSA})_2$ /diglyme solution, which is calculated by the area ratio of CV, was less than 20%. On the other hand, in 1 : 1 : 3 (mol) solution, the coulombic efficiency is improved with the cycle and almost 100% of the coulombic efficiency is achieved after 20 cycles, as shown in Fig. 5(b). The result will mean that diglyme is stabilized by solvating Mg^{2+} -ion in the solution and the reversible TFSA^- intercalation/de-intercalation was succeeded in the 1 : 1 : 3 (mol) solution. The reason of the improvement with the cycle is not clear, but we speculate some protective film will be formed on the graphite electrode. During the charge process (TFSA^-

Figure 3. (a) XRD pattern and (b) SEM image of the electro-deposits obtained by potential holding at -1.5 V (vs. Mg^{2+}/Mg) in $\text{Mg}(\text{TFSA})_2$: diglyme : HFE = 1 : 1 : 3 (mol).

Figure 4. Comparison of the anti-oxidation stability of (black) 0.5 mol dm^{-3} $\text{Mg}(\text{TFSA})_2/\text{diglyme}$ and (blue) $\text{Mg}(\text{TFSA})_2$: diglyme : HFE = 1 : 1 : 3 (mol). Scan rate was set at 5 mV sec^{-1} .

intercalation), Mg^{2+} -ion de-solvates to reduce Mg metal on the counter electrode. This means that free diglyme increases with the charge process, which will lead the oxidative decompose of free glyme on the graphite electrode. Therefore, we think the glyme or HFE derived deposit will play as the protecting film.

Figure 5. (a) Cyclic voltammograms of HOPG electrode and (b) the coulombic efficiency calculated from CVs in $\text{Mg}(\text{TFSA})_2/\text{diglyme}$ or $\text{Mg}(\text{TFSA})_2$: diglyme : HFE = 1 : 1 : 3 (mol).

The stability improvement is also confirmed by the OCP change for the charged state electrode. Figure 6(a) shows the OCP change after the potential holding at 4.3 V (vs. Mg^{2+}/Mg) for 50 hours. In 0.5 mol dm^{-3} $\text{Mg}(\text{TFSA})_2/\text{diglyme}$, OCP starts from as low as 3.5 V (vs. Mg^{2+}/Mg) and decreases to 3.0 V (vs. Mg^{2+}/Mg) immediately. The OCP of 3.5 V (vs. Mg^{2+}/Mg) corresponds to the oxidation potential of diglyme, which means the charged electrode decomposed the glyme solvents and the intercalated TFSA^- would no longer exist. On the other hand, the OCP maintained at 4.0 V (vs. Mg^{2+}/Mg) in the 1 : 1 : 3 (mol) solution, indicating the charged HOPG is stable in the solution. In fact, as shown in Fig. 6(b), XRD pattern for the charged HOPG indicates the disappearance of the characteristic peak of HOPG at 26.6° and the appearance of some new peaks. The periodic repeat distance (I_c) is represented by the following equation.

$$I_c = d_i + (n - 1) 3.354 \text{ \AA}$$

Where, d_i and n denote the gallery height and stage number, respectively. According to the Miller indices in the figure, stage 2

Figure 6. (a) OCP change after potential holding at 4.3 V for 50 hours and (b) XRD pattern of the TFSA[−] anion intercalated HOPG.

GIC with $I_c = 1.15$ nm and $d_i = 0.825$ nm is confirmed. The values show good accordance with the previous reports about TFSA[−] GIC²² and therefore, we can conclude the reversible TFSA[−] anion intercalation/de-intercalation into/from graphite electrode was succeeded in the glyme based solutions with the diluent by maintaining the solvate ionic liquid condition.

As mentioned in 3.1, the solvent shared ion pair and the contact ion paired TFSA[−] coexist in the 1 : 1 : 3 (mol) solution. So far, we've studied the interfacial Li⁺-ion transfer mechanism in the concentrated solution and cleared that the contact ion pair showed the stronger interaction than the solvent shared ion pair.³² Therefore, in the 1 : 1 : 3 (mol) solution, the TFSA[−] anion with the solvent shared ion pair condition will intercalate preferentially. Note that the result of Raman spectroscopy is different from the Li⁺-ion case, in which, TFSA[−] anion mainly remains as free anion in the diluted solutions. The difference will be caused by the favorable coordination number; four for Li⁺-ion and six for Mg²⁺-ion.¹³ Diglyme used in the study has only three oxygen in the structure, so the Mg²⁺-ion tends to interact with TFSA[−] anion directly to form ion pair in the Mg²⁺ : diglyme = 1 : 1 (mol) solutions.

Figure 7(a) shows the charge-discharge profile of the composite electrode with the three electrode cell. The discharge capacity for the 1st cycle shows about 70 mA h g^{−1} and almost no capacity fading is

Figure 7. Charge-discharge profile of graphite electrode in Mg(TFSA)₂ : diglyme : HFE = 1 : 1 : 3 (mol). (a) three electrode cell and (b) two electrode cell measurement.

confirmed in the following cycles. On the other hand, all charge curves do not reach the cut off potential and shows the experimentally set capacity of 100 mA h g^{−1}. The result will mean that the side reaction, i.e., the oxidative decomposition of the electrolyte solution also takes place with TFSA[−] intercalation. The relatively poor coulombic efficiency until around 10th cycles is also observed in CV, as shown in Fig. 5. We speculate that the protecting film is formed during the cycles, as discussed above.

As shown in Fig. 7(a), the graphite electrode exhibits the discharge plateau at around 3.4 V (vs. Mg²⁺/Mg) and over 70 mA h g^{−1} capacity at 333 K, which means the energy density of 230 mW g^{−1} (graphite) is expected. Apparently, the result seems to be comparable with those of the spinel oxides, such as MgCo₂O₄ and MgMn₂O₄,¹⁷ but these oxide electrodes require high temperature (generally over 373 K) to show the efficient capacity and operating electrode potential. From the results, we can conclude the TFSA[−] intercalation/de-intercalation reaction is more kinetically attractive than oxide materials.

Finally, the charge-discharge performance of a two-electrode cell consisting of Mg/1 : 1 : 3 (mol) solution/graphite was studied. As discussed above, Mg electrode shows the poor reversibility and

large stripping overpotential in the 1 : 1 : 3 (mol) solution, so the battery performance is expected to be much inferior to the result of three electrode measurement. Figure 7(b) shows the charge-discharge profile of the two-electrode cell. The discharge voltage plateau decreases to 2 V due to the large overpotential for the Mg stripping reaction. Note that the discharge capacity of 40 mA h g^{-1} (graphite) is obtained at every cycle, which means the Mg stripping reaction occurs repeatedly even after the charge process, i.e., the Mg plating reaction. Apparently, the result seems to be inconsistent with that in Fig. 2(c), but as discussed in Fig. 2, the passivation will occur when the large overpotential is applied for the Mg plating reaction and the continuous Mg stripping reaction is essentially able to take place in the 1 : 1 : 3 (mol) solution. So the overvoltage applied to the Mg negative electrode will be relatively small and therefore, the Mg stripping reaction will occur in all cycles. From the results and discussion above, we can conclude that the TFSA[−] anion intercalation/de-intercalation reaction will become a promising candidate for Mg secondary batteries, but the optimization of the diluents must be required.

4. Conclusions

In the present study, we focused on the anion intercalation reaction at the graphite electrode, aiming at the development of 3 V class Mg secondary batteries. In order to improve the anti-oxidation capability of the glyme based solutions, we used the Mg^{2+} : glyme = 1 : 1 (mol) solution with HFE as the diluents. Almost 100% coulombic efficiency was achieved and also obtained ca. 3.4 V (vs. Mg^{2+}/Mg) of discharge profile with the capacity of 70 mA h g^{-1} . On the other hand, the reversibility of the Mg plating/stripping reaction was quite poor, so now we are searching for the appropriate diluents or other solvent species. The detail will be reported elsewhere.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.20-00099>.

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