Plastic crystal-incorporated magnesium ion conducting gel polymer electrolyte for battery application

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Abstract. Studies on a novel composition of magnesium ion conducting gel polymer electrolyte (GPE), comprising a solution of Mg-salt, magnesium trifluoromethanesulfonate (Mg-triflate or $\text{Mg}(\text{Tf})_2$) in a plastic crystal succinonitrile (SN), entrapped in a host polymer poly(vinylidene fluoride–hexafluoropropylene) (PVdF–HFP) was reported. Small amount of an ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf) was added to stabilize the GPE composition. The electrolyte possesses excellent dimensional integrity in the form of free-standing thick film, which offers the ionic conductivity of $4 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature $\sim 26^\circ\text{C}$. The electrochemical potential window of the electrolyte, observed from the linear sweep voltammetry, is determined to be $\sim 4.1 \text{ V}$. The magnesium ion conduction in the GPE film is confirmed from cyclic voltammetry, electrochemical impedance spectroscopy and dc polarization techniques. Different structural, thermal and electrochemical studies demonstrate the promising characteristics of the polymer film, suitable as electrolyte in rechargeable magnesium batteries. The potential of the GPE as electrolyte/separator was ascertained by fabricating a prototype magnesium battery of the configuration $\text{Mg}:\text{graphite composite anode}/\text{GPE}/\text{MnO}_2\text{-cathode}$. The specific discharge capacity of 40 mAh g^{-1} (with respect to the MnO_2 cathode material) was obtained at the first discharge. The cell shows charge–discharge performance for eight cycles with a substantial fading in capacity.

Keywords. Gel polymer electrolyte; plastic crystal; succinonitrile; magnesium ion conduction; ionic liquid; magnesium battery.

1. Introduction

During the last few decades, cheap and environmental friendly energy storage/conversion devices with high energy density are in great demand. Interest is growing in the development of compact, light-weight batteries for portable appliances, such as cellular telephones and laptop computers. Rechargeable lithium batteries using lithium anode was studied for long time because lithium metal has high volumetric capacity i.e., 2061 mAh cm^{-3} and high electrochemical reduction potential (-3.04 V vs. saturated hydrogen electrode (SHE) [1]). However, there exist some inherent limitations in the Li-metal batteries including the followings: (i) lithium metal is highly reactive, which leads to the passivation layer formation at electrode–electrolyte interfaces, resulting an increase in internal resistance, (ii) it is highly corrosive and gets hydrolysed quickly, which leads to the problem of handling and safety, and (iii) it is prone to fast dendritic growth in the electrolyte region. Research is continued in the search of an alternative to the lithium batteries. Magnesium, possessing high volumetric capacity of $\sim 3833 \text{ mAh cm}^{-3}$ [1], high melting point (649°C) and electrochemical reduction potential of -2.3 V vs. SHE, emerges out as an alternative to the lithium battery anode. Further attractive features of magnesium are its low-cost, natural abundance and environment friendly nature for safe handling. Several research groups tried to develop

primary and nonaqueous Mg batteries [2–15]. Aurbach and coworkers [16] have developed a high-capacity rechargeable magnesium battery using electrolyte solutions based on Mg–organohaloaluminate salts. The same group reported that Chevrel phases of Mo_6T_8 ($\text{T} = \text{S, Se}$) can insert Mg^{2+} ions reversibly and can be used as cathode materials for rechargeable Mg-batteries [16].

Despite the various advantages of Mg as anode, the research and development on rechargeable Mg-batteries was retarded due to the problems including, (i) the difficulties associated with the reversibility of Mg-negative electrode due to its passivating character, and (ii) lack of the suitable Mg^{2+} ion conducting non-aqueous electrolytes. There are few reports on the polymer-based solid electrolytes consisting of poly(ethylene oxide) (PEO) with Mg salts [17–19]. The ionic conductivity values ranging from 10^{-6} to $10^{-4} \text{ S cm}^{-1}$, are reported for PEO–Mg salt complexes, however, the Mg^{2+} ion transport numbers of such systems are very low. Gel polymer electrolytes (GPEs) were recently considered as the most promising practical electrolytes of Mg-batteries for their excellent properties, such as flexible nature, improved safety and high Mg^{2+} ion conduction [20]. A copolymer of vinylidene fluoride and hexafluoropropylene (VdF–HFP) is one of the most potential matrices as host polymer to form GPE as it has relatively lower crystalline nature due to the copolymerization effect between VdF and

HFP in comparison with poly(vinylidene fluoride) (PVdF). In addition, HFP amorphous phase facilitates fast ionic conduction and VdF crystalline phase acts as a mechanical support for the membrane [21]. There are numerous reports on PVdF–HFP based GPEs, useful as electrolytes/separators in the development of solid state lithium, sodium and magnesium batteries and supercapacitors [20,22,23]. Although the room temperature conductivity values of the GPEs are significantly high due to the use of liquid components like ethylene carbonate (EC) and propylene carbonate (PC), they exist with significant drawbacks of flammability and volatility. To overcome these problems, ionic liquids were used, which allow the formation of much safer, high ion conducting, wide electrochemical window and thermally stable GPEs for Mg batteries [20]. However, the main drawback of ionic liquid-based polymer electrolytes is the complexities in ionic conduction owing to the mobility of component ions of the ionic liquids [19].

Recently, some polymer-based electrolytes were reported to be incorporated with plastic crystalline material, succinonitrile (SN), in which the plastic crystal acts as a solid solvent [19,24]. SN has attractive features like high polarity and high dielectric constant (~ 55 at room temperature), which ensure its ability to dissolve various types of salts and hence, increases the ionic conductivity [25]. SN-based electrolytes are highly conducting in its plastic crystalline phase between -38°C (the transition from normal to plastic-crystalline phase, T_{pc}) and 57°C (melting point of SN, T_{m}) due to the presence of orientational disorder (trans-gauge conformation) [26]. SN has vanishingly small vapour pressure, useful to avoid the electrolyte evaporation and it has reduced flammability [24].

In this work, we report the studies on a novel PVdF–HFP-based GPE entrapping the solution of magnesium trifluoromethanesulfonate [$\text{Mg}(\text{Tf})_2$] in plastic crystal SN. Small amount of ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf) was incorporated to obtain the stable GPE film. The thermal, structural and electrochemical properties of the GPE film were studied using various physical techniques including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV). A prototype Mg-cell was assembled comprising Mg–graphite composite anode, optimized GPE film as electrolyte and MnO_2 cathode. The performance of the cell was evaluated by charge–discharge tests for various cycles.

2. Experimental

2.1 Materials

PVdF–HFP ($M_w \sim 400,000$), EMITf (purity $\geq 98\%$), $\text{Mg}(\text{Tf})_2$ (purity 97%) and succinonitrile (purity 99%) were

obtained from Sigma-Aldrich. Magnesium powder and manganese dioxide (MnO_2) were obtained from Fluka. PVdF–HFP and ionic liquid EMITf were used as received. SN was further purified by recrystallization process and the salt $\text{Mg}(\text{Tf})_2$, Mg powder and MnO_2 were vacuum-dried at 100°C overnight before use. For the electrochemical measurements, the stainless steel (SS) sheets (Alfa Aesar, grade 304) were used as blocking electrodes. The circular discs of magnesium electrodes (area $\sim 1.2\text{ cm}^2$) were prepared by pressing the magnesium powder (Aldrich) at 4 tons cm^{-2} to use them as reversible electrodes. These discs were polished with successive grades of emery paper for a smooth finishing, then washed thoroughly in acetone and dried in vacuum.

2.2 Preparation of gel polymer electrolytes

The films of pure PVdF–HFP, PVdF–HFP/SN composite, GPEs containing Mg-salt, $\text{Mg}(\text{Tf})_2$ in SN were prepared by using ‘solution-cast’ method. The GPE film was prepared by dissolving 5 mol% (0.7 g) of $\text{Mg}(\text{Tf})_2$ in melted SN (3.3 g) in a sealed conical flask. The polymer PVdF–HFP (1 g) was separately dissolved in acetone (20 ml). The Mg-salt/SN mixture was stirred thoroughly and ultrasonicated for 15 min to ensure a homogeneous mixing. The mixture was then added to PVdF–HFP/acetone solution and stirred magnetically further for $\sim 24\text{ h}$. The solution was poured in glass Petri dish and the common solvent acetone was allowed to evaporate slowly at room temperature until a free-standing GPE film was obtained. The film was peeled off from the dish and stored in dry atmosphere. It was noticed that after few days of storage, the GPE film shows a phase separation. A small amount of powder-like material got separated on its surface and appeared to be the mixture of SN and Mg-salt. To avoid this phase separation and to obtain stabilized GPE, 1 mol% (0.13 g) of ionic liquid EMITf was added, while preparing the GPE film. As a result, a homogeneous and flexible GPE film was produced, which shows no phase separation even after its storage for several days. Finally, the composition of the GPE is referred as 20% PVdF–HFP + 80% ((5 mol% $\text{Mg}(\text{Tf})_2$ + 1 mol% EMITf) in SN) (w/w). Figure 1 shows the photograph of a typical PVdF–HFP/SN/ $\text{Mg}(\text{Tf})_2$ /EMITf GPE film. The films of pure PVdF–HFP and PVdF–HFP/SN (1:4 w/w) composite system were also prepared for comparison following the ‘solution-cast’ method. All these films were thoroughly vacuum-dried for several days before characterization.

2.3 Characterization techniques for GPE film

Thermal studies of the materials were carried out by TGA and DSC. TGA was done using a Perkin Elmer TGA system (TGA-7) in dry nitrogen atmosphere from room temperature to 550°C at the heating rate of $10^\circ\text{C min}^{-1}$. DSC measurements were performed under static nitrogen atmosphere using the calorimeter of TA Instruments (model: Q100). The samples were loaded in low-mass aluminium pans and

Figure 1. Photograph of a typical GPE film.

measurements were taken from -90 to 200°C at the heating rate of $5^{\circ}\text{C min}^{-1}$. The XRD patterns of the films were recorded using XRF (model: D8 DISCOVER, Brucker) at the scan rate of 2° per minute in the Bragg angle (2θ) ranging from 5 to 80° . FESEM (Mira-3, TESCAN) was used to investigate the morphology of PVdF-HFP/SN composite and GPE film. The SEM micrographs were taken at low vacuum after sputtering the samples with gold to prepare conductive surface.

EIS studies were carried out to evaluate the ionic conductivity using Broadband Dielectric/Impedance Analyzer (C-50 Alpha A, Novocontrol, Germany) in the frequency range from 1 MHz to 1 Hz . The conductivity measurements were performed by sandwiching the electrolyte film between two symmetrical SS sheets in the temperature range from -50 to 80°C . The electrochemical studies were performed by CV and LSV using an electrochemical analyzer (model: 660E, CH Instruments, USA). The dc polarization measurements were carried out for two cells with the symmetrical configuration using SS and Mg electrodes, namely, SS|GPE film|SS and Mg|GPE film|Mg. These cells were polarized by applying a dc voltage of 0.75 V .

2.4 Mg-battery fabrication and characterization

A magnesium battery was fabricated by using the GPE film as separator-cum-electrolyte. Mg-graphite composite anode was prepared by pressing the mixture of magnesium powder and graphite in the ratio of $4:1\text{ w/w}$ at a pressure 4 tons cm^{-2} . A cathode sheet was prepared by spin coating the mixture of MnO_2 ($70\text{ wt\%}$), graphite powder ($20\text{ wt\%}$) and the PVdF-HFP gel composition ($10\text{ wt\%}$). The mixture was thoroughly mixed in a mortar and spread on flexible graphite sheet ($250\text{ }\mu\text{m}$ thick, Nickunj Eximp Pvt. Ltd., India). The cathode sheet was vacuum-dried at $\sim 100^{\circ}\text{C}$ before its use in battery fabrication. Graphite powder acted as a conducting medium to provide electronic conductivity

to the electrodes. The cell: Mg:graphite anode/GPE/ MnO_2 cathode was stacked in a specially designed sealed container. The charge-discharge behaviour of the Mg-batteries was characterized using charge-discharge unit (model: BT-2000, Arbin Instruments, USA).

3. Results and discussion

3.1 Thermal studies

To test the thermal stability range and different possible phase changes in GPEs, the TGA and DSC studies were performed. Figure 2 shows the comparative TGA curves of pure PVdF-HFP, pure SN, PVdF-HFP/SN composite and the GPE, PVdF-HFP/SN/ $\text{Mg}(\text{Tf})_2$ /EMITf. No weight loss was observed for pure PVdF-HFP film (figure 2a) over a wide temperature range from room temperature to $\sim 420^{\circ}\text{C}$. Pure SN is stable up to $\sim 100^{\circ}\text{C}$ and evaporates fully at 216°C (figure 2b). The PVdF-HFP/SN composite (figure 2c) shows marginal weight loss of $\sim 2\text{ wt\%}$ up to $\sim 100^{\circ}\text{C}$, which is attributed to the loss of moisture adsorbed by the material, primarily SN. A substantial weight loss after $\sim 100^{\circ}\text{C}$ was observed due to the evaporation of SN. Similarly, weight loss of $\sim 5\text{ wt\%}$ up to 100°C was observed in the GPE, PVdF-HFP/SN/ $\text{Mg}(\text{Tf})_2$ /EMITf (figure 2d). This loss is also attributed to loss of water vapour, which is due to the presence of hydrophilic Mg-salt and ionic liquid EMITf. The analysis indicates that the GPE shows stability up to $\sim 100^{\circ}\text{C}$.

The comparative DSC thermograms of pure PVdF-HFP, pure SN, PVdF-HFP/SN composite, SN/ $\text{Mg}(\text{Tf})_2$ and the GPE, PVdF-HFP/SN/ $\text{Mg}(\text{Tf})_2$ /EMITf are shown in figure 3. Pure PVdF-HFP shows an endothermic melting peak at

Figure 2. TGA curves of (a) pure PVdF-HFP, (b) pure SN, (c) PVdF-HFP/SN composite and (d) PVdF-HFP/SN/ $\text{Mg}(\text{Tf})_2$ /EMITf GPE.

Figure 3. DSC curves of (a) pure PVdF-HFP, (b) pure SN, (c) PVdF-HFP/SN composite, (d) SN/Mg(Tf)₂ system and (e) PVdF-HFP/SN/Mg(Tf)₂/EMITf GPE.

~145°C (figure 3a). Pure SN shows two characteristic peaks at ~-38 and ~58°C (figure 3b), corresponding to its normal to plastic crystalline phase transition (T_{pc}) temperature and melting temperature T_m , respectively [27]. When ~80 wt% of SN is added to PVdF-HFP (figure 3c), the melting peak of PVdF-HFP was shifted to ~121°C. Two characteristic peaks of SN at T_{pc} and T_m persist in PVdF-HFP/SN system, indicating its composite nature as concluded from XRD also discussed later. On the addition of Mg(Tf)₂ in SN (figure 3d), a significant change in melting peak of SN was observed. The melting peak was downshifted to 33°C, while the peak at T_{pc} remains unaffected. The shift in melting peak T_m is due to the solvating ability of SN [27], indicating the interaction of nitrile group of SN with Mg-salt. Further, the intensity of the melting peak was substantially reduced, which indicates the increase in amorphous content due to the addition of Mg(Tf)₂ in SN.

On the addition of Mg(Tf)₂ and EMITf in SN, and immobilization of this Mg(Tf)₂/EMITf/SN system in PVdF-HFP to form GPE-film (figure 3e), the melting peak of complexed SN was splitted into two relatively broad peaks, centered at ~29 and 41°C. These two peaks are attributed to the melting of SN complexed with Mg-salt and IL both i.e., the coordination of nitrile group of SN with Mg²⁺ and EMI⁺ cations. Further, the melting peak at ~126°C indicates the presence of PVdF-HFP in GPE with its semi-crystalline nature. Furthermore, the presence of sharp peaks at T_{pc} ~ -37°C shows the phase transition of SN-complex from normal (monoclinic) phase to partially crystalline (cubic) and partially amorphous phases in GPE.

Figure 4. XRD patterns of (a) pure PVdF-HFP, (b) pure SN, (c) PVdF-HFP/SN composite and (d) PVdF-HFP/SN/Mg(Tf)₂/EMITf GPE.

3.2 Structural/morphological studies

To study the structural/morphological changes due to the addition of SN in PVdF-HFP and the addition of Mg(Tf)₂/EMITf in PVdF-HFP/SN host to form GPE, the comparative XRD and FESEM studies were performed. Figure 4 shows the comparative XRD patterns recorded for pure PVdF-HFP, pure SN, PVdF-HFP/SN (20:80 w/w) system and the GPE, PVdF-HFP/SN/Mg(Tf)₂/EMITf. The presence of XRD peaks in pure PVdF-HFP at 2θ ~17.9, 19.8, 26.9, 38.4, 39.2, 44.7, 65 and 78° (figure 4a) indicates its semi-crystalline nature i.e., the coexistence of mixed crystalline and amorphous nature. Pure SN shows the sharp characteristic peaks at ~19.7 and ~28° (figure 4b), corresponding to (110) and (200) planes, respectively [28]. When 20 wt% of PVdF-HFP is added in SN (figure 4c), the characteristic peaks of SN retain and no shift in the peak positions was observed. Some characteristics peaks of PVdF-HFP at 38.4, 39.2, 44.7, 65 and 78° were also observed distinctly. This shows the composite nature of the PVdF-HFP/SN system. In addition, a broad and intense hallow was observed between 10 and 40°, over which the sharp crystalline peaks are overlapped, which indicates a substantial amorphous nature of the PVdF-HFP/SN composite system.

The XRD pattern of the GPE shows almost similar pattern to the PVdF-HFP/SN composite with two sharp characteristic

Figure 5. SEM images of (a) PVdF-HFP/SN composite and (b) PVdF-HFP/SN/Mg(Tf)₂/EMITf GPE.

peaks of SN along with some weak XRD peaks of PVdF-HFP (figure 4d). This indicates that plastic crystalline phase of SN still persists even after the addition of Mg(Tf)₂ salt and small amount of ionic liquid, EMITf to form GPE. The GPE also shows a broad hallow between 10 and 40°, indicating the partial, but substantial proportion of amorphous nature in the GPE. Further, no peaks related with the salt Mg(Tf)₂ is observed in the XRD pattern of GPE (figure 4d), which indicates its complete dissolution in the SN/EMITf/PVdF-HFP system.

Figure 5a and b shows the comparative FESEM images of the PVdF-HFP composite and the GPE films. The PVdF-HFP/SN composite film is seen to have fibrous texture at the microscopic level (figure 5a). The plastic crystal SN appears to be uniformly distributed in the form of fine fibres, entrapped in the polymeric network. When Mg-salt/EMITf is added in PVdF-HFP/SN system to form GPE (figure 5b), the fibres of SN are distinctly seen to be swollen, immobilizing the salt/EMITf mixture.

Figure 6. Temperature dependent ionic conductivity of PVdF-HFP/SN/Mg(Tf)₂/EMITf GPE.

relationship, given by:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right), \quad (1)$$

where σ_0 is the pre-exponential factor and E_a the activation energy. The activation energy values before and after the transition in the GPE were evaluated and found to be ~ 0.908 and ~ 0.104 eV, respectively.

The electrochemical stability window, ESW (i.e., working voltage range) of the PVdF-HFP/SN/Mg(Tf)₂/EMITf GPE film was evaluated using LSV tested on the cell:SS|GPE|Mg. Here, the SS was employed as a working electrode and Mg as both the counter and the reference electrodes. The film was observed to be electrochemically stable up to ~ 4.1 V [29], as

3.3 Electrochemical properties

3.3a Ionic conductivity and electrochemical stability: The ionic conductivity of GPE, PVdF-HFP/SN/Mg(Tf)₂/EMITf was found to be $\sim 4 \times 10^{-3}$ S cm⁻¹ at room temperature ($\sim 26^\circ\text{C}$). The order of conductivity indicates the suitability of GPE as a substitute of liquid electrolyte to be used in Mg-batteries. Figure 6 shows the temperature-dependent ionic conductivity (i.e., $\log \sigma$ vs. $1/T$ plot) of the GPE. The onset of a fast jump in the $\log \sigma$ vs. $1/T$ plot is observed at $\sim 40^\circ\text{C}$, which corresponds to the onset of the melting of SN (figure 3). The linear variation in $\log \sigma$ vs. $1/T$ plot was observed before and after this transition, which can be described by Arrhenius

Figure 7. Linear sweep voltammogram of SS|GPE|Mg cell recorded at the scan rate of 5 mV s^{-1} at room temperature.

observed from the LSV pattern (figure 7). This is a sufficient voltage range for the applications in electrochemical devices, particularly, for the Mg-batteries.

3.3b Mg^{2+} ion conduction: EIS, CV and polarization: To confirm the Mg^{2+} ion conduction and reversibility of Mg/Mg^{2+} in PVdF–HFP/SN/Mg(Tf)₂/EMITf GPE medium, EIS, CV and dc polarization studies were performed at room temperature. Figure 8A shows the comparative impedance plots for the symmetrical cells, Cell-I: SS|GPE|SS (Cell-I) and Cell-II: Mg|GPE|Mg (Cell-II). The gel film was in contact with SS in Cell-I as blocking electrodes, whereas the pellets of Mg-powder were used as reversible (non-blocking) electrodes in Cell-II. The impedance plot of Cell-II shows a semicircular pattern, while the Cell-I shows steeply rising impedance pattern, indicating the blocking (capacitive) behaviour of ion storage at interfaces. The presence of semi-circle in Cell-II suggests that the electrochemical equilibrium is attained between Mg-electrodes and Mg^{2+} -ions in the GPE [30]. The comparative behaviour of the two cells is an indirect evidence of Mg^{2+} -ion conduction in the GPE under the present studies.

Mg^{2+} -ion conduction in the GPE film is confirmed from CV. CV patterns of the two cells (Cell-I and Cell-II) were recorded at room temperature at a scan rate of 5 mV s^{-1} , as shown in figure 8B. In Cell-II, cathodic and anodic peaks are distinctly observed, while no such peaks are observed in Cell-I. Also, the magnitude of currents are much higher in Cell-II as compared to Cell-I. Higher values of cathodic and anodic currents in Cell-II corresponds to the cathodic deposition and anodic oxidation of Mg at the electrode–electrolyte interfaces and the equilibrium attained by Mg^{2+} -ion at the interfaces

Figure 8. (A) EIS plots, (B) CV patterns and (C) dc polarization curves for (a) Cell-I: SS|GPE|SS (SS stands for stainless steel sheet) and (b) Cell-II: Mg|GPE|Mg (Mg stands for pressed pellet of Mg powder).

Figure 9. (a) Charge–discharge curves of the cell: Mg/GPE/MnO₂, recorded at room temperature. The number of charge–discharge cycles is marked on each curve, and (b) discharge capacity of the above cell as a function of charge–discharge cycles.

following the reversible reaction:

Such comparative behaviour of CV responses of Cell-I and Cell-II is the further evidence of Mg²⁺ conduction in the present GPE.

To further confirm the Mg²⁺ ion conduction in the GPE film, the polarization experiments were performed on the cells: Cell-I (SS/SS) and Cell-II (Mg/Mg). The polarization (current vs. time) curves for the cells are shown in figure 8c. For the Cell-I (with SS electrodes), the polarization current decreases rapidly and it approaches to the value close to zero. The ionic transport number (t_{ion}), was evaluated to be >0.99 [31]. The value of t_{ion} and the variation of polarization curve indicate the predominant ionic conduction in the

electrolyte. For the Cell-II (with the reversible Mg electrodes), the current steeply decreases initially and a steady state value is reached after a sufficient time of polarization. The steady state is obtained due to constant supply of Mg²⁺ ions from positive electrode and their dissolution in the negative Mg-electrode. This further confirms the conduction of Mg²⁺ ions through the GPE film.

3.3c Mg/MnO₂ battery: discharge capacity: To demonstrate the applicability of GPE (under the present study) as an electrolyte in Mg-rechargeable batteries, a cell Mg/GPE/MnO₂ was fabricated and characterized. As previously mentioned, Mg-anode is the composite of Mg and graphite powders in the ratio of 4:1 (w/w) in the form of pressed pellet, whereas the spin-coated cathode of MnO₂ contains graphite powder (20 wt%) and GPE (10 wt%). The Mg/MnO₂ cell shows open circuit voltage (OCV) of ~1.73 V. The cell was equilibrated for >2 h before its charge–discharge test at a constant current. Figure 9a shows the charge–discharge curves of the cell at a constant current of 38 μA cm⁻². The discharge curves show initial dips followed by the plateaus with respect to discharge capacity indicating facile Mg²⁺ ions insertion into MnO₂ structure from GPE. The specific discharge capacity of 40 mAh g⁻¹ (with respect to the MnO₂ cathode material) was obtained at the first discharge. The reversibility of the cell was fairly good although the discharge and recharge capacities of the cell were gradually decreased with respect to charge–discharge cycles (figure 9b). The discharge capacity abruptly decreased at second cycle and gradually increased in between with subsequent cycling. Capacity decline with cycling is attributed to the Mg/GPE interface, where the passivating surface film grows during the repeated cyclings. Also, high interfacial resistance at Mg-anode is thought to be responsible for poor reversibility of the Mg/GPE/MnO₂ cell [12,14,32].

4. Conclusions

A new magnesium ion conducting GPE film comprising the solution of Mg(Tf)₂ in SN immobilized in a host polymer PVdF–HFP was prepared, characterized and tested its applicability in Mg-battery. A small amount (1 mol%) of room temperature ionic liquid EMITf was added to obtain stable film of GPE. Various morphological, thermal and electrochemical studies were performed. The gel electrolyte film is found to be flexible, free-standing and transparent with excellent mechanical stability. The GPE offers high ionic conductivity of ~4 × 10⁻³ S cm⁻¹ at room temperature (~26°C) with a wider electrochemical stability window of ~4.1 V. The electrochemical equilibrium between Mg and Mg²⁺ ions occurs and hence, magnesium ion conduction in the GPE is confirmed from the EIS, CV and dc polarization techniques. A magnesium battery of configuration Mg:graphite/GPE/MnO₂:graphite:GPE was assembled and characterized with charge–discharge tests up to eight cycles. The first discharge capacity is found to be

40 mAh g⁻¹ of MnO₂. Further cycling of the cell leads to a decrease in capacity, which is possibly due to the passivation of Mg-anode. Efforts for further improvement in discharge capacity and cycle life of the magnesium batteries are continued.

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