

All-solid-state polymer electrolyte with plastic crystal materials for rechargeable magnesium battery

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ABSTRACT

In this paper, we report the synthesis and properties of a series of composite polymer electrolytes formed by dispersion of a non-ionic organic plastic material succinonitrile (SN) into poly (vinyl alcohol) complexed with magnesium acid salt. The addition of SN greatly enhances ionic conductivities of the electrolytes which is due to the high polarity and diffusivity of SN. The Mg²⁺ ion conduction is confirmed from impedance spectroscopy and transport number measurements. The highest conducting sample in the plasticized system was used to fabricate magnesium battery with configuration Mg/SPE/TiO₂. The discharge capacity of the fabricated battery was 17.5 mAh/gm.

Keywords: polymer electrolyte, succinonitrile

1 INTRODUCTION

Recent battery engineering has examined a number of new electrochemical systems using novel electrode materials and electrolytes. Magnesium has been considered as one such potential alternative to current battery electrode materials. It is a low cost, light and abundant element, environmentally benign and relatively easy to handle [1]. Electrochemically, magnesium has a high theoretical specific charge capacity (2205 A h/kg) [2] and high theoretical energy density (3.8 A h/cm³), making it an excellent candidate as a metal battery anode. Magnesium batteries have previously been described in [3-6].

Solid ionic conductors or solid electrolyte have some advantages in replacing liquid electrolyte, such as eliminating leakage and wide application including electrochemical display devices, power sources and so on. In spite of the attractive advantages of conventional solid electrolytes, one of the difficulties is the loss of contact between electrode and electrolyte because of dimensional changes during the charge-discharge cycles of the battery [7].

Polymer electrolytes PE possess the advantage of flexibility over inorganic solids. The use of all solid polymer electrolytes would overcome the limitations of liquid electrolytes, negate the need of separator and be processed easily [8].

It has been reported that in the plastic crystalline phase of highly polar succinonitrile (SN), various salts can be dissolved to give solid electrolytes with high ionic conductivities over a wide temperature range [9-11]. The presence of plasticity (i.e. easy deformation without fracture under applied stress [12]) in SN and its high degree of polarity provides a novel opportunity to develop composite polymeric systems involving plastic crystal as a solid plasticizer [13].

Heteropolyacids (HPAs) are one of the most attractive inorganic modifiers because these inorganic materials in crystalline form have been demonstrated to be highly conductive and structure stable. Phosphotungstic acid PWA is one of the strongest Keggin-type heteropolyacids exhibited preferential transport for positively charged ions [14], and it was highly probable that the described conductor is magnesium conducting because magnesium will be was one of the mobile species present in our system.

Owing to these merits, our current work is aimed at improving the electrical and electrochemical properties of the polymer electrolyte (PVA)/(MgBr₂) through doping in different proportions of phosphotungstic acid (PWA) and succinonitrile (SN). Ionic conductivity studies are performed on the solid polymer electrolyte. With a polymer electrolyte PE of optimum composition, solid-state Mg/PE/TiO₂ cell is assembled, and its cycling performances will be briefly examined to evaluate the applicability of the solid polymer electrolyte to solid-state magnesium batteries. Also, we investigated the discharge process of Mg/TiO₂ using scanning electron microscopy (SEM), and energy dispersive X-ray spectrometer (EDX).

2 EXPERIMENTAL SECTION

Poly (vinyl alcohol), PVA (degree of hydrolization $\geq 98\%$, Mw=72,000), magnesium bromide MgBr₂ and phosphotungstic acid (PWA) were received from Sigma. The complex electrolytes were prepared by mixing of 0.4% hydroquinone (antioxidant) (w/v), 1% (w/v) ethylene carbonate, PVA, MgBr₂ and PWA at several stoichiometric ratios in distilled water to get PVA_(1-x)(MgBr₂)_{x/2}(PWA)_{x/2} complex electrolytes, where x is 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 gm. The solutions with variable ratio were stirred vigorously and casted in Petri dish following solution cast technique at room temperature. To the highest conducting

composition in the polymer – acid salt system, different amount of SN (x') were added to produce the plasticized electrolyte system.

Conductivity measurements were made for PVA_(1-x)(MgBr₂)_{x/2}(PWA)_{x/2} composite polymer membrane by an ac impedance method. Samples of diameter 0.5 cm were sandwiched between the two similar brass electrodes of a spring-loaded sample holder. The whole assembly was placed in a furnace monitored by a temperature controller. The rate of heating was adjusted to be 2 K min⁻¹. Impedance measurements were performed on PM 6304 programmable automatic RCL (Philips) meter in the frequency ranging from 100 Hz to 100 kHz at different temperatures.

Magnesium transference number ($t_{Mg^{2+}}$) was measured by the steady-state technique which involved a combination of ac and dc measurements. The ac complex impedance response of the Mg/electrolyte/Mg cell was first measured to determine the cell resistances. It was followed by the dc polarization run, in which a small voltage pulse ($\Delta V=0.3V$) was applied to the cell until the polarization current reached the steady-state I_s . Finally, the ac impedance response of the cell was measured a gain to determine the cell resistance after dc polarization. Then $t_{Mg^{2+}}$ could be calculated with the following equation [15]:

$$t_{mg^{2+}} = \frac{I_s (\Delta V - R_o I_o)}{I_o (\Delta V - R_s I_s)} \quad (1)$$

where I_o and I_s are the initial and final steady-state currents and R_o and R_s are the cell resistances before and after the polarization, respectively.

Electrodes with 70:30% TiO₂ /graphite and 20% electrolyte were prepared using the following protocol. A slurry obtained by mixing the TiO₂ /graphite / electrolyte solution was cast. The electrode was prepared by cold pressing 0.6 gm into a pellet of 13 mm in diameter under 2.5 tons/cm². The optimum electrolyte were deposited on the cathode substrate with a spin coater at 5000 rpm. The anode was prepared by cold pressing 0.6 gm magnesium ribbon into a pellet of 13 mm in diameter under 2.5 tons/cm². Two-electrodes Swagelok test cell were assembled, the cell was discharged at room temperature on a multi-channel battery test system (NEWARE BTS-TC35) to analyze the electrochemical responses. The current density was 100 $\mu A/cm^2$.

Elemental mapping of the TiO₂ electrode was measured using an energy dispersive spectrometer (INCA Energy, Oxford Instruments) before and after discharge. Scanning electron microscopy (SEM) was used to observe changes in the surface morphology of the TiO₂ electrode before and after discharge.

3 RESULTS AND DISCUSSION

A typical result of dc and ac measurement for determining $t_{Mg^{2+}}$ for (PVA_(0.5)(MgBr₂)_{0.25}(PWA)_{0.25})/7.5 wt.% SN polymer electrolyte is shown in Fig. 1. The dc polarization current needs about 3 h to reach the steady state. After dc polarization, R_o increases from 5×10^4 to $7 \times 10^4 \Omega$. The value of $t_{Mg^{2+}}$, is evaluated using Eq. 1, has been found to be $\cong 0.67$ at room temperature.

Fig. 2 shows the Cole – Cole plot for PVA_(1-x)(MgBr₂)_{x/2}(PWA)_{x/2} (Fig. 2(a)) and plasticizers (PVA)_{0.5}(PWA)_{0.25}(MgBr₂)_{0.25}/SN (Fig. 2(b)) polymer electrolyte at 293k. The Cole-Cole plot for PVA_(1-x)(MgBr₂)_{x/2}(PWA)_{x/2} shows semicircle implying that the material is partially resistive and capacitive. However, samples containing both acid salt and SN show low frequency spike is due to the diffusion process. The ionic

conductivity is calculated according to $\sigma_b = \frac{1}{R_b} \times \frac{L}{A}$,

where L is the thickness of the polymer electrolyte film, A is the surface area of the film and R_b is the bulk electrical resistance value, which can be calculated from the intercept on the Z' axis.

The effect of acid salt (PWA) (MgBr₂) composition on ionic conductivity of pure PVA film is shown in Fig. 3a. The conductivity of pure PVA film is low about 10^{-10} S. cm⁻¹ at room temperature. The ionic conductivity is observed to increase gradually until 10^{-7} S. cm⁻¹ when 40 wt.% acid salt was added. The increase in conductivity is attributable to the increase in acid salt content which can dissociate to provide more mobile ion as more acid salt is added, which contributes to increase in conductivity. The effect of SN on ionic conductivity of (PVA)_{0.5}(PWA)_{0.25}(MgBr₂)_{0.25} is shown in Fig. 3b.

The conductivity of (PVA)_{0.5}(PWA)_{0.25}(MgBr₂)_{0.25} is low about 10^{-7} S. cm⁻¹ at room temperature. The ionic conductivity is observed to increase gradually until 10^{-6} S. cm⁻¹ when 10 wt.% SN was added. The ionic conductivity enhancement can be attributed to the decrease in crystallinity of (PVA)_{0.5}(PWA)_{0.25}(MgBr₂)_{0.25} polymer electrolyte as well as the high polarity and diffusivity of SN.

The first discharge curves of a Mg/electrolyte /TiO₂ cell at room temperature is given in Fig. 4. The Mg/electrolyte/TiO₂ cell shows a discharge capacity 17.5 mAh/gm. An investigation was made of surface of the TiO₂ electrode by means of SEM, and EDX in order to determine the reaction in the electrodes. The SEM morphology of the original TiO₂ electrode before discharge is given in Fig. 5 a. The surface consists of a homogenous mixing of powders such as TiO₂, graphite, and electrolyte materials (20%). The surface of electrode after discharge (Fig. 5 b) is smooth and covered with materials that are product of reactants, such as

Mg_xTiO_2 . Table 1 lists EDX results for the TiO_2 electrodes before and after discharge. After discharge the contents of magnesium increase from 0.78% to 6.34% in the TiO_2 electrodes. The content of oxygen decreases from 27.91% to 24.80%. The ratio of magnesium to titanium is about 0.394%, therefore the final product might be Mg_xTiO_2 .

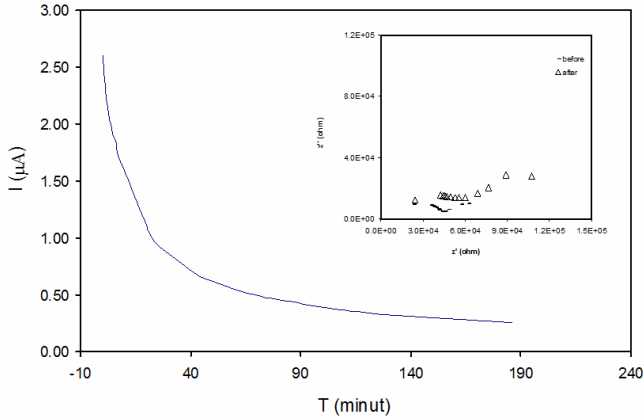


Figure 1: The dc polarization current of Mg/PE with 7.5 wt.% SN/Mg symmetric cell at 20 °C, where the inset shows the ac complex impedance before and after dc polarization.

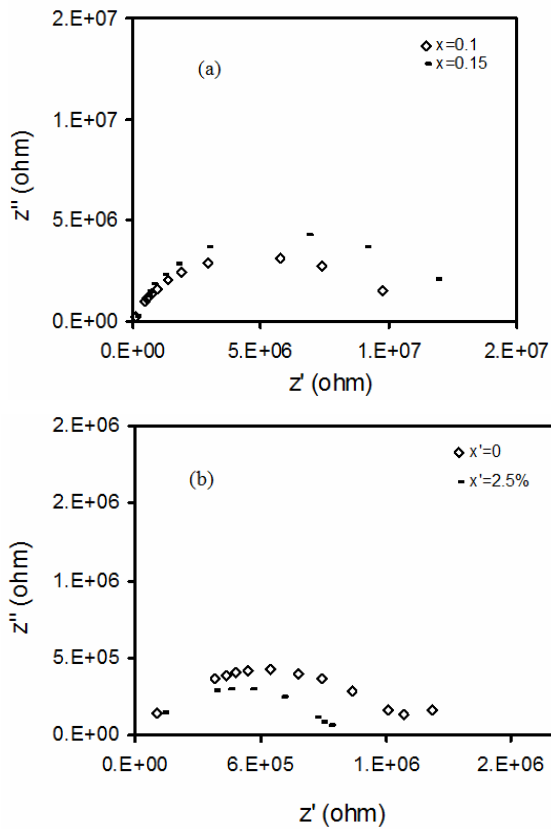


Figure2: Cole Cole plots for $PVA_{(1-x)}(MgBr_2)_{x/2} PWA_{(x/2)}SN_{(x)}$ films (a) $x=0.1, 0.15, x'=0$, (b) $x=0.5, x'=0, 2.5$

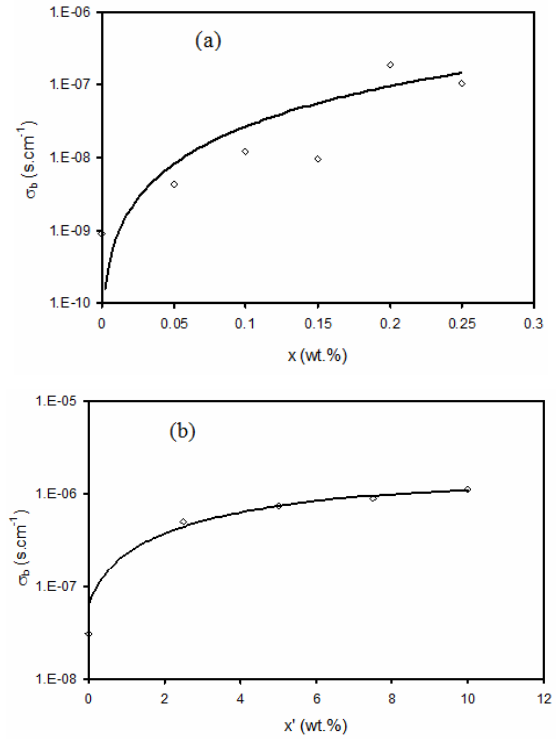


Figure 3: the ionic conductivity of PVA with various concentrations of (a) $x'=0$ and $x \neq 0$, (b) $x=0.5$ and $x' \neq 0$

4 CONCLUSION

We successfully demonstrated the approach of combining a polymer and a plastic crystal to generate a new type of magnesium ion conductor.

The result can summarized as follow:

- 1- The addition of SN can obviously increase the free volume of the polymer electrolyte, thus enhances the ionic conductivity of the polymer. Further optimization with regard to materials processing and choice of acid salt and polymer would lead to possible application of the present plastic. polymer composites for magnesium battery.
- 2- The ionic conductivity depended on the content of SN. The highest conductivity of the PE examined was $\approx 10^{-5} S. cm^{-1}$ (at 20 °C) for the composition of 10 wt.% SN.
- 3- The cell capacity of $TiO_2/PE/Mg$ is 17.5 mAh/gm.

5 ACKNOWLEDGMENT

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Wt %		At %		Element	
Discharge	Normal	Discharge	Normal		
34.76	26.74	53.43	46.00	K	C
24.80	27.91	30.37	36.04	K	O
6.34	0.78	5.11	0.66	K	Mg
---	0.36	---	0.24	K	P
16.09	34.88	6.58	15.05	K	Ti
---	0.81	---	0.30	K	Fe
2.84	3.32	0.30	0.37	L	W
17.17	5.23	4.21	1.35	K	Br
100.00	100.00	100.00	100.00	Total	

Table 1: EDX results of TiO₂ electrode before and after discharge.

REFERENCES

- [1] I. J. Polmear, Light Alloys, third ed., Edward Arnold, London, 1995.
- [2] J.O. Besenhard, M. Winter, ChemPhysChem 3 (2002) 155.
- [3] B. Winther-Jensen, M. Gaadingwe, D.R. MacFarlane, M. Forsyth, Electrochim. Acta 53 (2008) 5881.
- [4] S. Sathyanarayana, N. Munichandraiah, J. Appl. Electrochem. 11 (1981) 33.
- [5] W. Li, C. Li, C. Zhou, H. Ma, J. Chen, Angew. Chem., Int. Ed. 45 (2006) 6009.
- [6] Timothy Khoo, Patrick C. Howlett, Maureen Tsagouria, Douglas R. MacFarlane, Maria Forsyth, Electrochimica Acta 58 (2011) 583–588
- [7] Fenton DE, Parker JM, Wright PV. Polymer 1973;14: 589–592.
- [8] Shuhua Zhou, Shibi Fang, European Polymer Journal 43 (2007) 3695–3700
- [9] P.J. Alarco, Y. Abu-Lebdeh, A. Abouimrane, M. Armand, Nat. Mater. 3 (2004) 476.
- [10] S. Long, D.R. MacFarlane, M. Forsyth, Solid State Ionics 161 (2003) 105.
- [11] P.J. Alarco, Y. Abu-Lebdeh, A. Abouimrane, M. Armand, Nat. Mater. 3 (2004) 476.
- [12] J. Sherwood (Ed.), The Plastically Crystalline State, Wiley, London, 1979.
- [13] Li-Zhen Fan, Joachim Maier, Electrochemistry Communications 8 (2006) 1753–1756,
- [14] Zhiying Li, Yang Liu, Hongtao Liu, Ping He, Qian Zhang, Jinghong Li Solid State Ionics, 177,(2006)1281-1286.
- [15] G. P. pandey, R. C. Agrwal, S. A. Hashmi, J. Solid State Electrochemistry,2011.

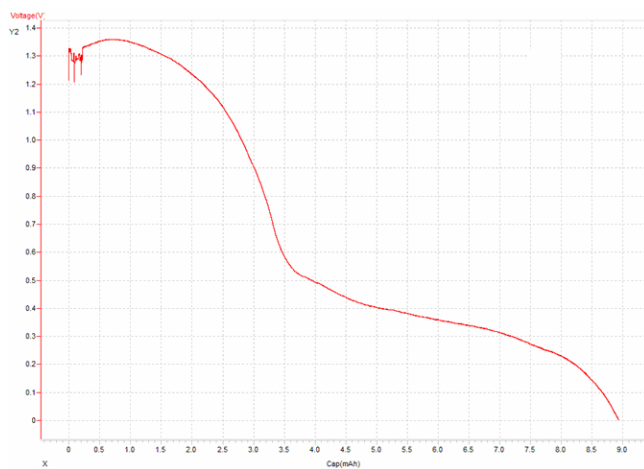


Figure 4: Discharge curve of Mg/PE/TiO₂ cell.

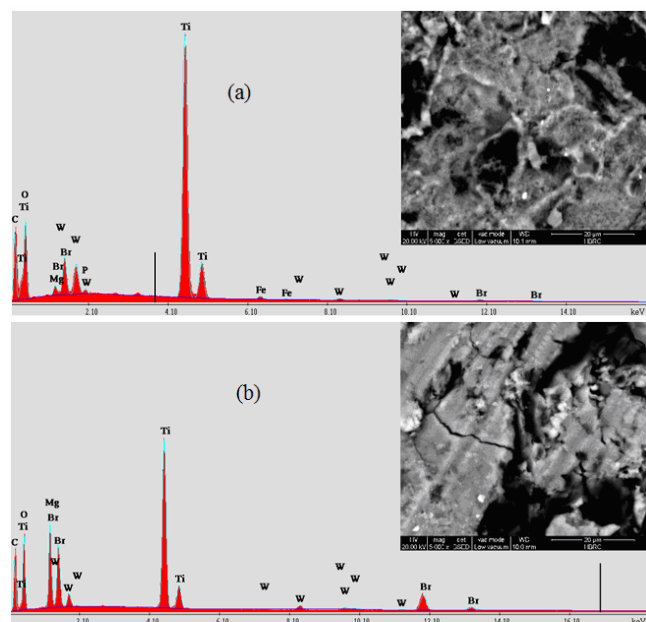


Figure 5: EDAX & SEM images of Titanium dioxide electrode (a) before discharge, (b) after the first discharge