Magnesium Ion Conducting Polymer Electrolytes: Potential Alternative as Non-lithium Electrolytes for All-Solid-State Battery Application

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ABSTRACT

Majority of the portable batteries for mobile applications are Li^+-ion polymer electrolyte/ Li-metal electrode batteries. These chemicals encounter several serious limitations while in use in electrochemical devices. To eliminate these limitations it has been strongly felt to look for alternate non-lithium electrolyte/ electrode systems. Mg^{2+}-ion salts/ Mg-metal electrodes have recently been reported as possible/ potential alternate primarily due to the fact that these chemicals have comparable electrochemical characteristics to those of lithium chemicals and relatively cheaper/ non toxic. The present paper reports the current status of Mg^{2+}-ion conducting polymer electrolyte materials including some new dry polymer electrolytes viz. Solid Polymer Electrolytes (SPEs)/ Nano Composite Polymer Electrolytes (NCPEs) synthesized by a novel hot-press technique at our laboratory along with characterization and All-Solid-State battery performance studies. These batteries performed quite satisfactorily under low current drain states.

Keywords: Non-lithium Polymer Electrolytes, Mg^{2+}-ion conducting SPE/ NCPE Films, All-Solid-State Battery.

1. INTRODUCTION

Solid Polymer Electrolytes (SPEs) are currently considered as potential alternative to liquid/ aqueous electrolytes. SPE in thin/ flexible form show tremendous technological promises to develop all-solid-state compact/ light weight/ leak-proof rechargeable batteries in variety of shapes/ sizes including mini/micro batteries [1-10]. Majority of the batteries used today in portable electronic devices are Li^+-ion batteries. They are based either on Li^+-salt electrolyte solution immobilized in inert polymer matrix or dry polymer-Li^+-salt complexes viz. 'Solid Polymer Electrolyte' (SPE)/ 'Nano Composite Polymer Electrolyte' (NCPE) films. SPE/NCPE film batteries can be potentially scaled-up to larger sizes to power EVs. Since 1990s , Li^+ -ion batteries have outperformed other conventional batteries viz. lead-acid, Ni-Cd, Ni-MH etc. [11, 12]. Fig. 1, illustrating Ragone plot for different battery systems, clearly indicates the superiority of Li^+- ion batteries over others [13]. However, Li^+-ion salts and Li-metal encounter many inherent problems. These chemicals are highly reactive/ toxic hence, difficult to handle in the open ambience; less environment friendly hence, disposal of waste is always a problem; less natural abundance hence, expensive. Besides, in the recent past there were some serious fire-hazards were reported while using these batteries. Very recently, Li^+-ion batteries in American 'Dreamliner' Jets exploded/ caught fire in-flight (Fig. 2) [14] and as a result all flights were grounded. Thus, looking to high priority safety concerns, the power sources based on Li^+-chemicals may involve serious risks and hence, some non-lithium electrolytes/ electrodes must be explored. In this regard, Mg^{2+} –ion salts and Mg–metal electrode have recently been looked upon as appropriate choice in place of Li^+-salt and Li-metal electrode [15, 16]. This is due to the fact that electrochemical characteristics viz. electrochemical equivalence, negative electrode potential as well as ionic radii of Mg^{2+}–salt/ Mg-metal and Li^+–ion salts/ Li–metal are quite comparable. Mg^{2+} -ion displaces twice as much charge as Li^+ -ion and the batteries based as Mg^{2+} -ion polymer electrolytes do not require intercalation electrodes as in case of Li^+ -ion rechargeable batteries. Moreover, Mg^+-salts Mg-metal are relatively inexpensive, abundantly available, non-toxic and very safe in use.

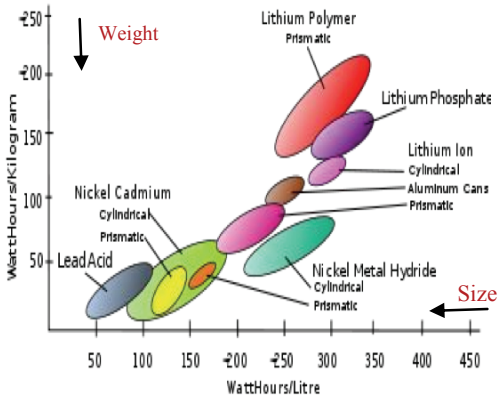

Fig. 1: Ragone plot for different battery systems [13].

We at the present research laboratory synthesized number of SPE/NCPE films using different Mg^{2+} - ion complexing salts [17, 18] and after identifying the optimum conducting films by characterizing their materials / ion transport properties, fabricated all-solid-state batteries. The present paper reports

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the electrochemical cell performance studies on these batteries.

Fig. 2 'Dreamliner Jet': Li-ion Battery exploded on-flight [14].

2. EXPERIMENTAL

SPE/NCPE films were cast by hot-press technique. This technique is relatively much quicker / inexpensive/ solution free/ dry procedure and can be preferred over the traditional solution–cast method. The details on both the casting procedures have appeared elsewhere in the literature [10, 17–20]. On the basis of materials/ion transport characterization studies, following SPE/NCPE films have been found to exhibit optimum room temperature conductivity value (σ_{rt}):

SPE/ NCPE Films	σ_{rt} (S/ cm)
SPE: [80PEO: 20Mg$(CF_3SO_3)_2$]	: ~ 3 x10^{-6}
SPE: [85PEO: 15 Mg $(ClO_4)_2$]	: ~3 x 10^{-6}
NCPE: [85PEO: 15Mg $(ClO_4)_2$] + 5% TiO_2	: ~ 1 x 10^{-5}
NCPE: [85PEO: 15Mg $(ClO_4)_2$] + 3% MgO(nano)	: ~ 1 x 10^{-5}
NCPE: [80PEO: 20Mg$(CF_3SO_3)_2$] + 4% TiO_2	: ~ 2 x 10^{-5}
NCPE: [80PEO: 20Mg$(CF_3SO_3)_2$] + 5% MgO(nano)	: ~ 2 x 10^{-5}

High purity/ precursor chemicals (Sigma-Aldrich, USA), used to cast SPE/ NCPE films, are: **Polymeric host:** Poly(ethylene oxide) PEO (Mw ~ 6 x 10^5), **Complexing salts:** (Magnesium trifluoromethane-sulphonate) Mg $(CF_3SO_2)_2$, Magnesium perchlorate $Mg(ClO_4)_2$ (purity > 99%), **Filler materials:** TiO_2 (>99%, <100 nm), MgO (>99%, <100 nm) as IInd–phase passive/active dispersoid, dispersed into Ist-phase SPE host to form NCPE films. Mg – metal powder (>99% Sigma-Aldrich) as anode and different cathode mixtures: ***(C + MnO_2 + Electrolyte) &(C + I_2 + Electrolyte)*** in thin pallet form were used to sandwiched the SPE/NCPE films to fabricate **All-Solid-State Batteries** in the cell configuration: ***Anode (Mg)// SPE/ NCPE film// Cathode.***

3. RESULTS AND DISCUSIONS

The Open Circuit Voltage (OCV) and cell potential discharge characteristics were studied at room temperature. Fig. 3 shows potential profiles for **Cell ## 1-12** when discharge through 100 KΩ load. Except for an initial and final drop due to well-known polarization build-up effect, the cell potentials remained practically flat for 100 hrs. Some important cell parameters have been evaluated from the plateau region of the discharge profiles and listed in Table 1 along with OCV values. All the batteries performed quite satisfactorily specially under low current drain states.

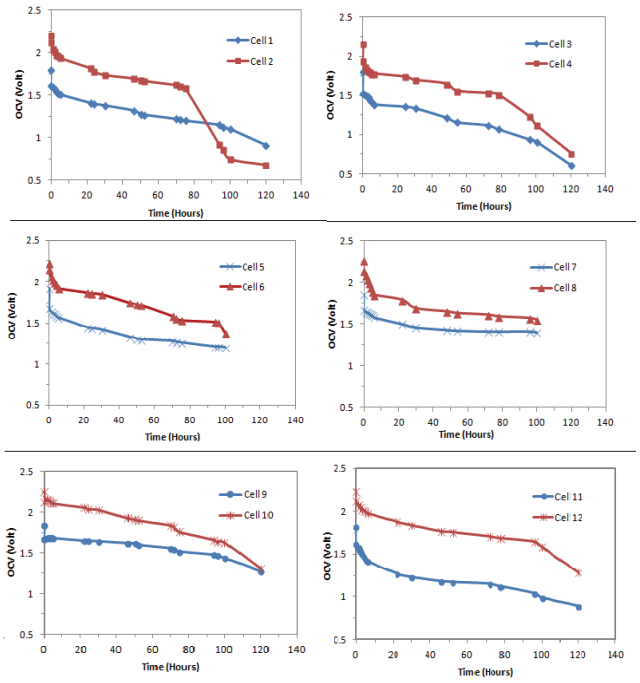

Fig. 3 Cell potential discharge profiles as a function of time:
Cell 1: Mg/[85PEO: 15Mg $(ClO_4)_2$/ C+MnO_2+Electrolyte;
Cell 2: Mg/ [85PEO: 15Mg $(ClO_4)_2$/ C+I_2+Electrolyte;
Cell 3: Mg/ [80 PEO: 20Mg $(CF_3SO_3)_2$]/ C+MnO_2+Electrolyte;
Cell 4: Mg/[80PEO: 20Mg $(CF_3SO_3)_2$]/ C+I_2+Electrolyte;
Cell 5: Mg/[85PEO: 15Mg $(ClO_4)_2$]+ 5TiO_2/ C+MnO_2+Electrolyte;
Cell 6: Mg/ [85PEO: 15Mg $(ClO_4)_2$] + 5TiO_2/ C+I_2+Electrolyte;
Cell 7: Mg/[80PEO: 20Mg$(CF_3SO_3)_2$] + 4TiO_2(nano)/ C+ MnO_2+ Electrolyte;
Cell 8: Mg/ [80PEO: 20Mg$(CF_3SO_3)_2$] + 4TiO_2(nano)/ C+I_2+ Electrolyte;
Cell 9: Mg/ [85PEO: 15Mg$(ClO_4)_2$] + 3MgO(nano)/ C+MnO_2+ Electrolyte;
Cell 10: Mg/ [85PEO: 15Mg $(ClO_4)_2$] + 3MgO(nano)/ C+I_2+ Electrolyte;
Cell 11: Mg/ [80PEO: 20Mg$(CF_3SO_3)_2$] + 5MgO(nano)/ C+ MnO_2 + Electrolyte;
Cell 12: Mg/ [85PEO: 15Mg $(ClO_4)_2$] + 3MgO/ C+I_2+Electrolyte.

Table 1 Some important cell parameters evaluated from the plateau region of the discharge profiles. All the cells were discharged though **100 KΩ** at room temperature. (For Cell Number please refer to the caption Fig. 3).

Cell	OCV (Volt)	Current Density ($\mu A/cm^2$)	Discharge Capacity (μAh)	Specific Power ($\mu W/g$)	Specific Energy (mWh/g)
Cell: 1	1.79	10.41	1046	15.32	1.15
Cell: 2	2.2	11.52	1428	15.14	1.72
Cell: 3	1.8	9.24	1220	25.92	2.59
Cell: 4	2.16	12.01	1520	25.12	2.41
Cell: 5	1.92	10.59	1420	16.13	1.61
Cell: 6	2.22	13.37	1765	24.29	2.42
Cell: 7	1.85	12.65	1670	27.33	3.28
Cell: 8	2.26	13.22	2094	29.59	3.55
Cell: 9	1.84	11.64	1560	16.90	1.69
Cell: 10	2.25	13.03	2064	20.23	2.43
Cell: 11	1.81	9.31	1230	26.59	2.66
Cell: 12	2.23	12.92	2046	27.79	3.33

4. CONCLUSION

All-Solid-State battery based on Mg^{2+}-ion conducting SPE/NCPE films have been fabricated and discharged through 100 KΩ load. All the batteries performed quite satisfactorily specially under low current drain states. Based on these studies it can be concluded that these newly synthesized Mg^{2+}-ion conducting SPE/ NCPE films: (the non-lithium Polymer Electrolytes) can be considered as potential alternate to Li^+ - ion salt polymer electrolytes for all-solid-state electrochemical device applications. However, what is needed urgently is to enhance the room temperature conductivity value of these SPE/NCPE film at least by 1-3 orders of magnitude. This can possibly be achieved if we introduce Nano–Ionic effects in these systems. This work is currently in progress at present Laboratory.

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