

Short communication

Improved performance of Li hybrid solid polymer electrolyte cells

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Abstract

The seminal research by Wright et al. on polyethylene oxide (PEO) solid polymer electrolyte (SPE) generated intense interest in all solid-state rechargeable lithium batteries. Following this a number of researchers have studied the physical, electrical and transport properties of thin film PEO electrolyte containing Li salt. These studies have clearly identified the limitations of the PEO electrolyte. Chief among the limitations are a low cation transport number (t_+), high crystallinity and segmental motion of the polymer chain, which carries the cation through the bulk electrolyte. While low t_+ leads to cell polarization and increase in cell resistance high T_g reduces conductivity at and around room temperatures. For example, the conductivity of PEO electrolyte containing lithium salt is $<10^{-7} \text{ S cm}^{-1}$ at room temperature. Although modified PEO electrolytes with lower T_g exhibited higher conductivity ($\sim 10^{-5} \text{ S cm}^{-1}$ at RT) the t_+ is still very low ~ 0.25 for lithium ion. Numerous other attempts to improving t_+ have met with limited success. The latest approach involves integrating nano domains of inorganic moieties, such as silicate, aluminosilicate, etc. within the polymer component. This approach yields an inorganic–organic component (OIC) based polymer electrolyte with higher conductivity and t_+ for Li^+ . This paper describes the improved electrical and electrochemical properties of OIC-based polymer electrolyte and cells containing Li anode with either a TiS_2 cathode or Mag-10 carbon electrode. Several solid polymer electrolytes derived from silicate OIC and salt-in-polymer constituent based on Li triflate (LiTf) and PEO are studied. A typical composition of the SPE investigated in this work consists of 600 kDa PEO, lithium triflate (LiTf, LiSO_3CF_3) and 55% of silicate based on (3-glycidoxypopyl)trimethoxysilane and tetramethoxysilane at molar ratio 4:1 and 0.65 mol% of aluminum(tri-*sec*-butoxide) (GTMOs-A11-900k-55%). Several pouch cells consisting of Li/OIC-based-SPE/cathode containing OIC-based-SPE-LiTf binder were fabricated and tested, these cells are called modified cells. The charge/discharge and impedance characteristics of the new cells (also called modified cells) are compared with that of the pouch cells containing the conventional PEO–LiTf electrolyte as the cathode binder, these cells are called non-modified cells. The new cells can be charged and discharged at 70 °C at higher currents. However, the old cells can be charged and discharged only at 80 °C or above and at lower currents. The cell impedance for the new cells is much lower than that for the old cells.

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1. Introduction

Of the three battery components (anode, cathode and electrolyte) the most critical and still unoptimized and under-developed is the electrolyte component. The polyethylene oxide (PEO)-based polymer electrolyte exhibits very low conductivity and cation transport number. These limitations are inherent to PEO electrolyte since:

- (1) ionic conduction occurs mainly in the liquid-like amorphous regions;
- (2) the cation of the salt is coordinated to the heteroatom in the polymer chain (in this case, oxygen atom);
- (3) cation conduction occurs by the segmental motion of the polymer chain;
- (4) low polymer dielectric constant ~ 6 (poor salt dissociation);
- (5) semi-crystallinity below 60 °C.

Several different approaches to enhancing the Li^+ conductivity, cation transport number, etc. in the PEO polymer system met with very limited success [1]. Recently, compos-

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ite solid polymer electrolytes (SPEs) made of an inorganic component along with a conventional salt-in-polymer electrolyte have received considerable attention due to suppression of PEO crystallization, enhancement of the mechanical properties, and often enhancement of conductivity and Li transference numbers [2]. All these parameters are important for successful application of these SPEs in secondary lithium batteries. Composite polymer electrolytes can be prepared in different ways, but all techniques can be placed into two major groups: (i) the inorganic component is preformed and then mixed with a polymer or (ii) the inorganic component is formed in situ within a polymer electrolyte. The former method can be represented by the incorporation of inorganic fillers (TiO_2 , Al_2O_3 , SiO_2 , etc.) [3] or clay platelets in polymers [4]. The latter method is represented by formation of metal oxides within a polymeric system, thus fresh interfaces between inorganic and polymer component are developed.

The influence of filler particles on the properties of composite polymer electrolytes has been described in the literature. As reported in several papers [5], decrease of the filler size from micron-scale to nanometer-scale yields a significant increase of surface-to-volume ratio and enhanced conductivity. There is an opinion that the major influence of filler particles is due to suppression of crystallization of the ‘PEO + Li salt’ phase, while the fully amorphous PEO shows no suppression of ion aggregation. According to a number of reports, the interface between the inorganic and polymeric components plays an important role in enhancement of the composite SPE properties. If this is a crucial factor, then formation of the inorganic component in situ should yield a ‘fresh’ interface, while the surface of conventional fillers may be modified with reagents used for their synthesis and stabilization. In situ formation of the inorganic component can result in nanoparticles or interpenetrating networks (or both) [6], thus providing the potential for higher conductivity and t_+ for Li^+ in the polymer system. These improved properties will help improve cell performance, operate cells at lower temperatures and higher currents, thus increasing the delivered power.

Studies on structure and properties of SPEs derived from aluminosilicate organic–inorganic component (OIC) and salt-in-polymer constituent based on polyethylene oxide and Li triflate (LiTf) were reported elsewhere [7]. OIC was prepared from (3-glycidoxypropyl)trimethoxysilane (GLYMO) and $\text{Al}(\text{tri-}i\text{-sec-butoxide})$ (AB) using hydrolytic condensation (or sol–gel reaction). Hydrolytic condensation of GLYMO and AB within PEO– LiTf component yields fresh OIC/PEO– LiTf interfaces with aluminosilica bearing different Si and Al sites closely mixed with the polymer. The glycidyl group of GLYMO ensures a good miscibility with PEO: this group is polymerized in the presence of $\text{Al}(\text{tri-}i\text{-sec-butoxide})$ giving oligo(ethylene oxide) chains and may react with terminal hydroxyl groups of PEO, which results in additional cross-linking within SPE. Compared to salt-in-polymer electrolytes, the composite SPEs based on aluminosilicates demonstrate enhanced properties. Here, we report the elec-

trical and the electrochemical properties of SPEs based on a fully siliceous OIC prepared from GLYMO and tetramethoxysilane (TMOS) in full cells. The full cell consists of $\text{Li}/\text{OIC-SPE}/\text{cathode binder}$. The cathode is either TiS_2 or Mag-10 carbon. We have investigated two types of full cells where the cathode binder is different. The cells that have the conventional PEO polymer SPE as cathode binder (called non-modified cells) and the cells that have the OIC–SPE as cathode binder (called modified cells).

2. Experimental

Poly(ethylene glycol) (PEG) and polyethylene oxide with molecular weights of 600 Da and 100 kDa, respectively, were purchased from Aldrich and used as received. Li triflate, tetrahydrofuran (THF), aluminum(*tri-sec*-butoxide), tetramethoxysilane (Aldrich), chloroform (EM Ind., Inc.), (3-glycidoxypropyl)trimethoxysilane (Fluka) were used without further purification. Water was purified with a ‘Barnstead NANOpure water’ purification system. The SPE synthesis was carried out as per the procedure published elsewhere [8].

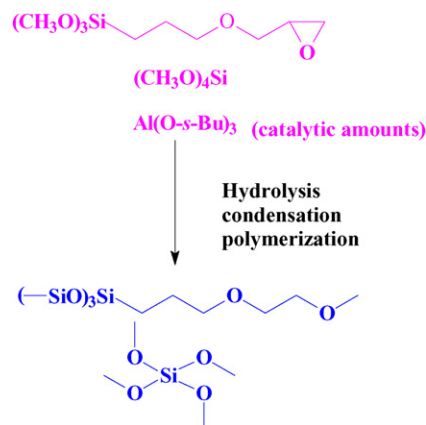
The equipment used for the evaluation of the physical properties of the SPE and the electrical and the electrochemical properties of the SPE and the full cells are described elsewhere [9].

3. Results and discussion

A line drawing of a typical structure of the OIC–SPE is shown below.

- (1) Since silicate component is made by TMOS and GLYMO (the latter containing an organic moiety), organically modified silica nanoparticles are formed (an organic–inorganic component).
- (2) The OIC is either tethered to polymer chain (for PEG) or located within the PEO component (for high molecular weight PEO). AB is added as a catalyst for glycidyl group polymerization.

The synthesis of the OIC (sol–gel techniques) is shown below



4. Characterization of polymer electrolyte

1. Structure: X-ray, transmission electron microscopy (TEM) and NMR studies show that the silicate material is amorphous, silica nanoparticles measure from 7 to 50 nm depending on the SPE composition and are located within mobile PEO domains.
2. Thermal properties: DSC of the salt/PEO/hybrid blends shows a glass transition near -50°C , which may vary for different compositions.
3. Conductivity: $\sim 3 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature has been achieved so far (~ 2 orders of magnitude higher than the conventional PEO electrolyte).
4. Transference #: Li cation transference number of ~ 0.8 has been achieved.

5. Characterization of full cell

5.1. Electrochemical performance

Electrochemical performances of full cells consisting of OIC-SPE sandwiched between Li anode and cathode were evaluated. A picture of a pouch cell is given below.



Picture of pouch cell containing Li anode, OIC-SPE electrolyte and TiS_2 cathode with binder

We used three types of binders for the cathode. For the non-modified cells we used the conventional PEO-LiTf (O:Li=8:1) and for the modified cells we used different composition of OIC-SPE: binder for TiS_2 (GTMOs-A11-TEA-1-900-40) and binder for Mag-10 carbon (GTMOs-A12-900-55). For the former, triethylamine was used as a catalyst for a sol-gel reaction, while for the latter, HCl was used.

Impedance was measured at different temperatures between 25 and 80°C . In Figs. 1–3, are shown impedance for the non-modified and modified cells.

In Figs. 1 and 2, are shown Nyquist plot of impedance for the non-modified and modified cells, respectively, containing TiS_2 cathodes. Remember that the non-modified cell consists of the conventional PEO-LiTf as the cathode binder and the modified cell contains OIC-SPE developed in this work as the cathode binder. The impedance plots clearly show that the impedance at 80°C for the non-modified cell is very high compared to that of the modified cell at a lower temperature (65°C). The lowering of impedance in the modified cell compared to the non-modified is related the replacement of PEO-LiTf with OIC-SPE, since this is the only difference

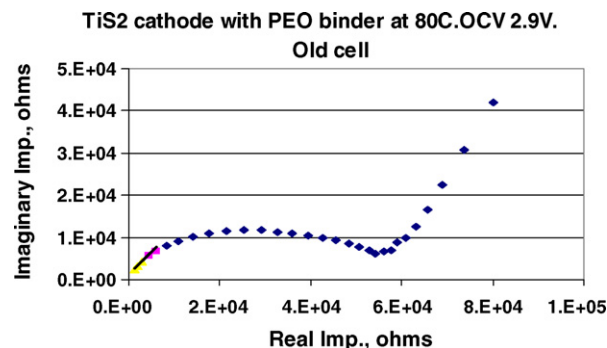


Fig. 1. Nyquist plot of impedance for Li/OIC-SPE/ TiS_2 with PEO binder (non-modified cell) at 80°C .

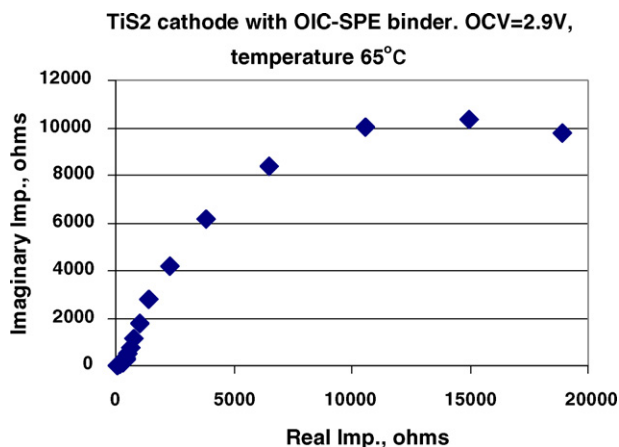


Fig. 2. Nyquist plot of impedance for Li/OIC-SPE/ TiS_2 , with OIC-SPE binder (modified cell) at 65°C .

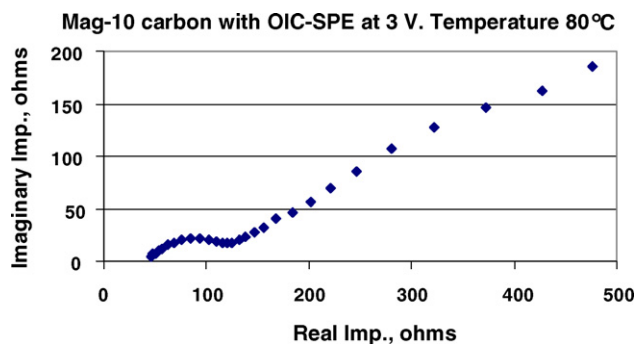


Fig. 3. Mag-10 carbon with OIC-SPE at 3 V (modified cell), temperature 80°C .

between the two cells. Similarly, the modified cell with Mag-10 carbon cathode shows lower impedance (Fig. 3) compared to that of the corresponding non-modified cell (not shown in the paper).

6. Charge/discharge characteristics

The non-modified cells were tested at 80°C , while the modified cells were tested at 70°C . The cells were kept at

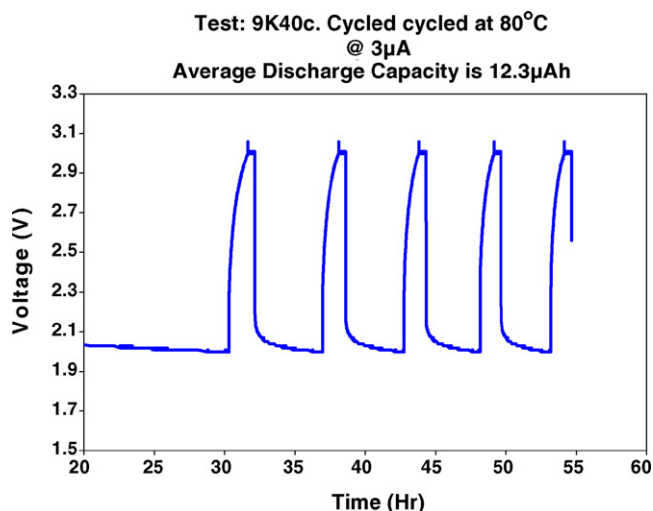


Fig. 4. Charge/discharge traces for the non-modified cell with TiS_2 cathode.

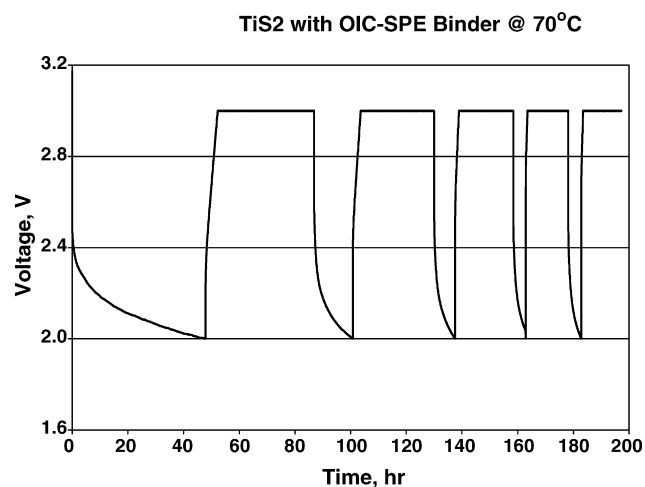


Fig. 5. Charge/discharge traces for the modified cell with TiS_2 cathode.

the desired temperature for a couple of hours before starting measurement. The cells were charged/discharged at different currents (shown in the figures). In Figs. 4–6, are shown charge/discharge traces for the non-modified and modified cells, respectively. The non-modified cell with TiS_2 cathode

Table 1
Discharge capacity for the old and new cells

Cell name	Discharge temperature ($^{\circ}\text{C}$)	Discharge current (μA)	Average discharge capacity (μAh)
Non-modified cell with TiS_2 cathode	80	3	12
Modified cell with TiS_2 cathode	70	10	55
Modified cell with Mag-10 cathode	70	50	53

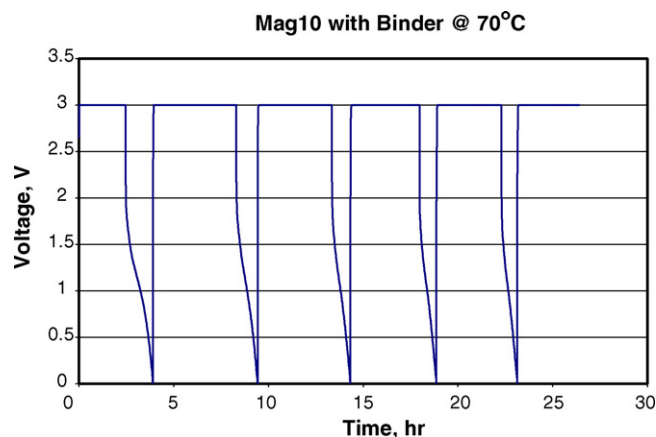


Fig. 6. Charge/discharge traces for the modified cell with Mag-10 cathode.

was discharged at $3 \mu\text{A}$ and at 80°C while the modified cell with TiS_2 cathode was discharge at $10 \mu\text{A}$ and at 70°C . We got even better results with the modified cell with Mag-10 as the cathode. This cell was discharged at $50 \mu\text{A}$ and 70°C . In Table 1, is shown the average discharge capacity for the three cells.

7. Conclusions

We have successfully synthesized OIC-SPE with improved electrical properties. The room temperature conductivity is $>10^{-5} \text{ S cm}^{-1}$, two orders of magnitude higher conductivity than the conventional PEO-SPE. We tested pouch cells containing PEO-LiTf and OIC-SPE as cathode binder. The modified cells gave more capacity at a higher rate and lower temperature than the non-modified cell.

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