



Short communication

Realization of high performance polycarbonate-based Li polymer batteries



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ABSTRACT

This work describes effective approaches to achieve high cell performance of solid-state Li polymer batteries based on high-molecular-weight poly(trimethylene carbonate) (PTMC). The origin of a gradual capacity increase observed during passive storage and/or active cycling in $\text{LiFePO}_4|\text{PTMC}_x|\text{LiTFSI}|\text{Li}$ cells was investigated by SEM/EDX, indicating an obvious penetration of the polymer electrolyte through the porous composite electrode at elevated temperatures. Refining the interfacial contacts at the electrode/electrolyte interface by adding PTMC oligomer as an interfacial mediator led to significant capacity enhancement already during initial cycles. Optimized cell performance was achieved through this method rather than other approaches, such as casting electrolyte directly onto the electrode and using a polyether oligomer. Successful long-term cycling stability and rate capability tests also resulted from the suggested strategy.

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1. Introduction

The increasing attention towards safety of rechargeable batteries and the hazards of flammable organic solvents used in commercial Li-ion batteries has directed research focus on components with increased safety and stability. Intense efforts have been devoted to studies on stabilizing the electrolyte/electrode interface to suppress side-reactions, such as introducing stable Li salts (e.g., LiFSI, LiBOB) [1,2] and functional additives (e.g., vinylene carbonate, allyl ethyl carbonate) [3–5]. Alternatively, Li-ion or Li batteries comprising chemically inert and mechanically robust solid polymer electrolytes (SPEs) have shown great potential to suppress the risks of a thermal runaway [6–9]. It is, however, well known that SPEs are associated with a number of problems limiting their implementation at cell level. Apart from the limited ionic conductivity, there is also a high interfacial resistance caused by the poor contact and wetting of SPEs on common composite electrodes.

Due to the slow segmental motion of polymer chains, the ionic conductivity of most polyether-based SPEs is commonly restricted to below 10^{-5} – 10^{-6} S cm^{-1} at ambient temperatures and 10^{-3} – 10^{-4} S cm^{-1} at 60 °C [8,10–12]. In the pursuit of high cell performance, including good rate capability, long-term cyclability and stability, alternative SPEs should possess more favorable properties not least in terms of ionic conductivity, but also enabling sufficient cationic diffusion and stable electrode/electrolyte interfaces to achieve fast charge/discharge and long lifespan. Within this context, polycarbonates – a high-molecular weight analogue to linear and cyclic carbonate solvents – have been considered promising polymer host candidates [13–17]. In our previous work on poly(trimethylene carbonate) (PTMC) [17], we demonstrated, for the

first time, battery cycling performance of such polycarbonate-based polymer electrolytes in LiFePO_4 half-cells at elevated temperature. However, the cycling profiles of PTMC-based SPEs displayed low initial capacity followed by a slow capacity increase during storage/cycling until reaching the full capacity of LiFePO_4 after 70 days.

This work reports further investigations to explore the origin of this unexpected cycling behavior. In addition, we establish a simple yet effective approach to refine the electrode/electrolyte interface by applying PTMC oligomers as interfacial mediators at the interface between the composite electrode and the SPE. Unlike conventional gel electrolytes which typically comprise great amounts of liquid solvents and plasticizers, acetate-terminated PTMC oligomer is highly viscous and is here used in combination with a PTMC-based SPE for LiFePO_4 half-cells. This should not only promote wetting of the SPE/electrode interface without compromising the interfacial stability, but also maintain the mechanical strength in the SPE as a physical separator. Cycling performance of Li-batteries based on the PTMC/salt SPEs using different salts (i.e., LiTFSI and LiBF_4) is compared at elevated temperature. Obvious improvement in the initial capacity was achieved in the Li polymer cells utilizing this strategy and promising overall long-term cell performance is demonstrated at different C-rates.

2. Experimental

2.1. Electrolyte preparation

Self-standing polymer electrolytes $\text{PTMC}_8|\text{LiTFSI}$ and $\text{PTMC}_5|\text{LiBF}_4$ were prepared by casting a homogeneous mixture of high-molecular-weight PTMC (synthesis details described elsewhere [17]) and Li salts (LiTFSI, Purolyte, from Ferro Corp. and LiBF_4 from Aldrich) in anhydrous acetonitrile (Acros Organics) in PTFE molds. For comparison, the

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electrolyte solution of PTMC₈LiTFSI was also cast directly onto the composite electrode to promote interfacial coverage. The solvent was evaporated under nitrogen flow for 3 days and residual solvent was further removed in a vacuum oven at 60 °C for 2 days. All operations were performed in an argon-filled glovebox (<1 ppm water, <10 ppm oxygen). The electrolyte thickness was determined within the range 150–200 μm and the water content in the as-formed electrolytes was estimated to around 35 ppm by Karl-Fischer titration.

2.2. Synthesis of PTMC oligomer

A hydroxyl-terminated PTMC oligomer, DP = 6, was synthesized through ring-opening polymerization of trimethylene carbonate using ethanol as initiator and 2-(dimethylamino)ethyl benzoate as a polymerization catalyst [18]. The end-groups were acetylated by reaction with triethylamine and acetyl chloride in tetrahydrofuran to produce acetate-terminated PTMC oligomer. The structure of the oligomer was confirmed through ¹H NMR.

2.3. Cell configuration

A pouch-cell configuration was used by sandwiching the electrolyte between the LiFePO₄ composite electrode (electrode preparation described elsewhere [17]) and a symmetrically positioned Li foil. The electrode used for cell assembly was around 12 ± 2 μm in thickness. Additionally, a small amount of PTMC oligomer was applied with sufficient coverage between the composite electrode and the solid electrolyte. A comparative cell was also prepared using poly(ethylene glycol) dimethyl ether (PEGDME, Mn ~ 500 from Aldrich and dried over 3 Å molecular sieves in the glovebox) and applied in the same manner as an interfacial mediator.

2.4. Morphology characterization

In order to investigate the penetration level of the polymer electrolyte through the composite electrode, one sample was carefully taken from the back side of the composite electrode which was in contact with the Al current collector, i.e., the furthest region of the bulk electrode from the LiFePO₄/SPE interface, after long-term cycling. The same area was collected from a pristine electrode for comparison. The electrode morphology was studied using a Zeiss Merlin scanning electron microscope (SEM) with Aztec energy-dispersive X-ray spectroscopy (EDX) system operating under a probe current of 80 μA and 10 keV with a working distance of about 8 mm.

2.5. Electrochemical characterization

All cells were stored at 60 °C for 3 h prior to cycling. Galvanostatic cycling was then performed at 60 °C (room temperature conductivity is too low for cell testing) between 2.7 and 3.7 V vs. Li⁺/Li at different C-rates (e.g., C/100, C/55, C/20, C/10, C/5) using a Digatron BTS-600 battery testing system. The cut-off voltage was chosen to minimize the influence of Al corrosion [19].

3. Results and discussion

As observed in earlier studies on the cycling behavior of self-standing electrolytes based on PTMC/LiTFSI in LiFePO₄ half-cells, a distinct capacity increase from less than 10 mAh g⁻¹ to around 153 mAh g⁻¹ is found during cycling and/or storage for at least two months at 60 °C [17]. This behavior is also seen in Fig. 1a, which displays the rate capability of cells comprising PTMC₈LiTFSI and PTMC₅LiBF₄ electrolytes, respectively. The latter material was previously studied by Silva et al. [15] and we have, through impedance measurements, determined that the ionic conductivities of these two electrolytes are very similar, i.e. 3 × 10⁻⁶ S cm⁻¹ for PTMC₈LiTFSI vs.

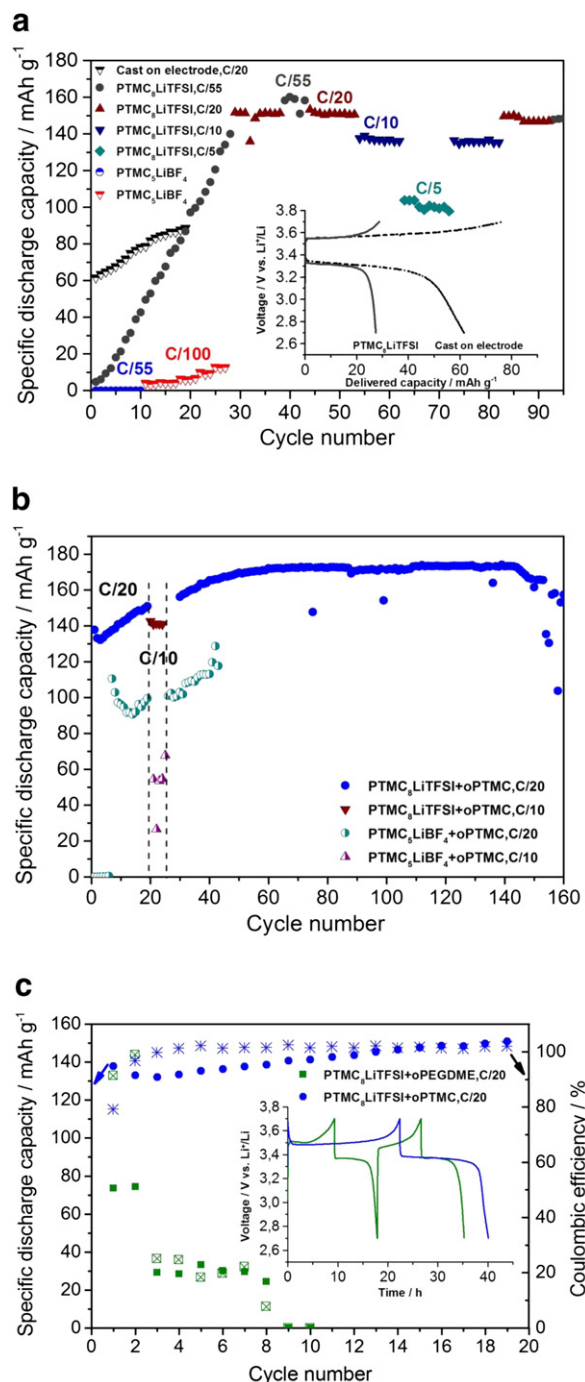


Fig. 1. Cycling performance of Li||LiFePO₄ cells using a) self-standing PTMC₈LiTFSI or PTMC₅LiBF₄ as compared with PTMC₈LiTFSI directly cast onto the composite electrode (inset illustrating the cycling profile of PTMC₈LiTFSI at C/20 during the 1st cycle); b) PTMC₈LiTFSI and PTMC₅LiBF₄ with PTMC oligomer (oPTMC) as an interfacial mediator at various C-rates at 60 °C; c) comparison of PTMC₈LiTFSI using different oligomers (oPTMC or oPEGDME) at C/20 and 60 °C (solid dots for discharge capacity and star dots for coulombic efficiency), the inset showing the cycling profile during initial cycles. It should be noted that inhomogeneity in the mass of Al current collectors (5.41 ± 0.08 mg, diameter of 11 mm) might result in slight variations in the estimated capacity.

2 × 10⁻⁶ S cm⁻¹ for PTMC₅LiBF₄, at 60 °C. However, cells containing PTMC₅LiBF₄ here display poor cycling behavior also for low C-rates such as C/55 and C/100. In comparison, PTMC₈LiTFSI turned out to be a better electrolyte in terms of rate performance, which could probably be due to the more favorable Li⁺-polymer dissociation and ion-pair suppression in the presence of the bulky TFSI anions [20]. Furthermore, as reported earlier from X-ray photoelectron spectroscopy (XPS)

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