



The interfacial evolution between polycarbonate-based polymer electrolyte and Li-metal anode

Chen Wang^{a,b}, Huanrui Zhang^a, Jiedong Li^a, Jingchao Chai^{a,b}, Shanmu Dong^{a,*}, Guanglei Cui^{a,*}

^a Qingdao Industrial Energy Storage Technology Institute, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, 266101, China

^b University of Chinese Academy of Sciences, No.19A Yuquan Road, Beijing, 100049, China

HIGHLIGHTS

- The origin of high ionic conductivity of polycarbonate-based polymer electrolytes.
- The interfacial evolution of Li metal/CPPC-SPE is illuminated.
- Cellulose could limit the interfacial degradation.

ARTICLE INFO

Keywords:
Interface
Evolution
Polymer electrolytes
Li-metal anode

ABSTRACT

Solid polymer electrolyte is strongly considered to be one of the key materials to solve safety problem of high energy lithium batteries caused by flammable liquid organic carbonate solvent, while the development and application of solid polymer electrolytes are seriously restricted by the low ambient temperature ionic conductivity. Recently, aliphatic polycarbonate-based electrolytes have been reported to possess high ionic conductivity at ambient temperature. Herein we choose poly (propylene carbonate) as a model to investigate the origin of the high ionic conductivity of polycarbonate-based polymer electrolytes. Our results prove that poly (propylene carbonate) degrades to micromolecular segments when contacts with Li-metal anode. The depolymerization products can infiltrate the interface and swell the electrolyte to develop the amorphous state so as to reduce both interfacial and bulk resistance. As scaffold of the electrolyte, cellulose can limit this reaction at the interface by physical obstruction. The hydroxyl units can also quench the lithium alkoxide intermediate to suppress further degradation, guaranteeing the security of the system. This study provides a profound understanding of the composition, reaction and evolution of the interface between polymer electrolyte and Li-metal anode, which sheds new light on the interface construction of ambient-temperature solid-state lithium metal batteries.

1. Introduction

Li-metal anode-based battery technologies have attracted scientists' wide attention in recent decades owing to their high specific energies [1–5]. However, the application of Li-metal anode is strictly limited for the safety hazards. Combustion of the flammable liquid organic carbonate solvent can be easily triggered by the internal short-circuit for the growth of lithium dendrite [6,7]. Solid-state lithium batteries, which replace the conventional flammable liquid electrolytes with non-flammable solid-state electrolytes, are considered to be the effective solution to the abovementioned problems [8–11]. Solid polymer electrolytes have been widely studied in recent years due to their strong flexibility, good processibility as well as high safety [12–14]. Among

them, poly (ethylene oxide) (PEO) was the most intensively investigated one due to its obvious advantage for simple and flexible battery design. While the highly crystalline structure of PEO could inhibit the migration of lithium ion, resulting in low ionic conductivity at room temperature [15–19]. Therefore, polymer electrolyte with high ionic conductivity at ambient temperature is in urgent need.

It worth noting that a class of aliphatic polycarbonates have been reported to possess high ionic conductivity at ambient temperature, which is viewed as promising alternative for polymer electrolyte. For example, Kimura et al. reported a kind of poly (ethylene carbonate)-based electrolyte (PEC-LiFSI 80 wt%) showed an ionic conductivity of the order of $10^{-5} \text{ S cm}^{-1}$ at 30 °C [20]. In our previous work, we had combined poly propylene carbonate (PPC) and cellulose nonwoven to

* Corresponding authors. No.189 Songling Road, Laoshan District, 266101, Qingdao, China.
E-mail addresses: dongsm@qibebt.ac.cn (S. Dong), cuijl@qibebt.ac.cn (G. Cui).

make an solid-state polymer electrolyte (CPPC-SPE) appropriate for ambient-temperature solid polymer lithium batteries. Such polymer electrolyte possesses an excellent ionic conductivity of $3.0 \times 10^{-4} \text{ S cm}^{-1}$ at 20°C [21], which is one order of magnitude higher than ether-based polymer electrolytes. However, the origin of this high ionic conductivity has rarely been explored.

In this work, CPPC-SPE was chosen as a typical polycarbonate-based polymer electrolyte to investigate the origin of unusual high ionic conductivity. We found a significant resistance decrease of CPPC-SPE when directly contacting to Li-metal at 80°C . This phenomenon illustrated the existence of interfacial reaction between the polymer electrolyte and Li-metal anode (the heating period at 80°C before cycling is called activation process as follows), which is exactly the determinant factor of ionic conductivity. The interfacial evolution through the activation process was identified due to the interfacial reaction with Li-metal. Furthermore, our results demonstrated that cellulose could limit the degradation to a beneficial extent at the interface, leading to the promotion of the system stability, integrity and security.

2. Results and discussion

2.1. The evolution of the interface

EIS testing was performed to monitor the impedance of Li/CPPC-SPE/Li and stainless-steel/CPPC-SPE/stainless-steel (SS/CPPC-SPE/SS) symmetrical cells every 2 h at the activation process of 80°C . Significant resistance change of Li/CPPC-SPE/Li symmetrical cells was observed as shown in Fig. 1a. It is evident that the resistance was still almost $7000 \Omega \text{ cm}^2$ [2] after 2 h, while it changed to $20 \Omega \text{ cm}^2$ [2] and reached a steady value after 16 h (Fig. 1a). In the initial stage, the high degree of crystallinity of PPC existed as the barriers for the mobile charge carriers and the contact of the interface between CPPC-SPE with Li-metal electrode was poor, give rise to the huge resistance value [22]. After the sufficient activation, the resistance dramatically decreased and finally reached a steady value ($20 \Omega \text{ cm}^2$ [2]). The tremendous resistance decrease indicated that there might exist some reactions between CPPC-SPE and Li-metal electrode through the activation process, which lead to the significant reduction of both the bulk resistance and the interfacial resistance. From the SEM images shown in Fig. 1c, the gap between CPPC-SPE and lithium electrode vanished and the contact

between them became tight after the sufficient activation process at 80°C . However, it was noticed that the impedance of CPPC-SPE measured in SS/CPPC-SPE/SS cell changed rarely until it reached a constant value after 5 h, which still remained at $10000 \Omega \text{ cm}^2$ (Fig. 1b). Here the high frequency semi-circle of the resistance spectra represented the bulk resistance of the polymer electrolyte, the low frequency region is attributed to an obvious polarization behavior due to the blocking electrodes [22]. In this process, the bulk resistance of PPC almost did not change, proved that the resistance decrease in Fig. 1a was aroused by the interfacial reaction between electrolyte and Li-metal electrode. These two processes were schematically portrayed in Fig. 1d. The contact between CPPC-SPE and Li-metal electrode becomes tight after sufficient activation at 80°C . While the CPPC-SPE and stainless steel are still independent from each other even after long-term contact for 24 h. Plenty of interspaces still exist at the interface between them. In this process, the interfacial reaction between Li-metal electrode and CPPC-SPE leads to the decrease of both bulk resistance and interface resistance. We found the same phenomenon in poly (2, 3-butylene carbonate) (PBC), poly ethylene carbonate (PEC) based solid polymer electrolyte, which are also typical aliphatic polycarbonate-based electrolytes. The resistance of Li/Li symmetrical batteries and SS/SS symmetrical batteries with PBC based polymer electrolyte (CPBC-SPE) and PEC based polymer electrolyte (CPEC-SPE) presented the same change tendency as CPPC-SPE based batteries, shown as Figure S1. This phenomenon confirmed the reaction between polycarbonate-based electrolyte and Li-metal electrode, which could remarkably improve the ionic conductivity by two ways. Firstly, the sectional degradation of the polymer decreased the crystallinity of the electrolytes, motivated the transference of Li^+ and reduced the bulk resistance of the electrolyte [23,24]. Secondly, the degradation products infiltrate the interface to improve the contact between electrolyte and lithium metal, reduce the interfacial resistance. This perspective would be further elucidated as follows.

2.2. Surface chemistry of the interface

To better elucidate the interface reaction between PPC based electrolyte and Li-metal electrode, Fourier transform infrared spectroscopy (FTIR) was employed to detect CPPC-SPE (PPC-LiTFSI-cellulose) before and after activation process. As well, to directly investigate the reaction

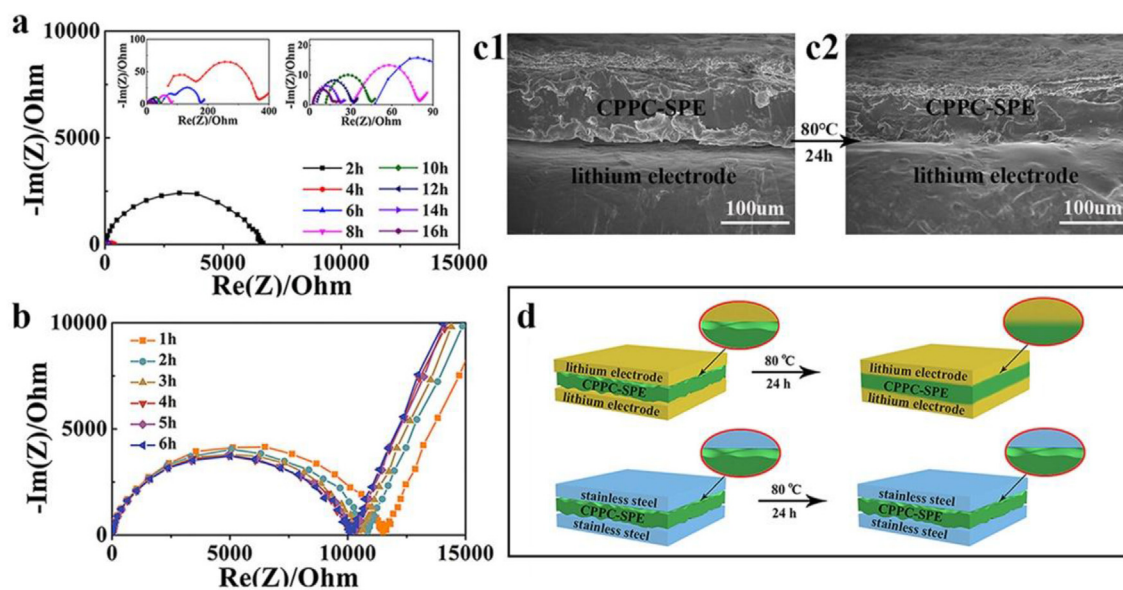


Fig. 1. The electrochemical impedance change of (a) Li/Li symmetrical battery and (b) SS/SS symmetrical battery with CPPC-SPE in the activation process at 80°C ; (c) Typical SEM images of the contact interface between CPPC-SPE and Li-metal electrode before and after activation; (d) The schematic diagram of the active processes of this two kind of batteries.

Download English Version:

<https://daneshyari.com/en/article/7724768>

Download Persian Version:

<https://daneshyari.com/article/7724768>

[Daneshyari.com](https://daneshyari.com)