Electrochemical impedance spectroscopy of a Li–S battery: Part 2. Influence of separator chemistry on the lithium electrode/electrolyte interface

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ABSTRACT

Asymmetric separators with polysulfide barrier properties, consisting of porous polypropylene (PP) grafted with styrene sulfonate (SS), PP-*g*-PLiSS, were characterized in symmetric Li/Li cells using electrochemical impedance spectroscopy to investigate the influence of separator chemistry on the Li electrode/electrolyte interface. The symmetric Li/Li cell approach was found to be applicable for probing the transport properties of the separator and, therefore, determining the role of the functionality added to the separator. Electrolyte resistance and the formation of a surface film on metallic Li were both monitored as functions of time and the concentration of cation-exchange groups introduced at and near the surface of one side of the separator (expressed as the graft level). No continuous build-up of Li electrode/electrolyte interface resistance was observed, indicating that the addition of a cation-exchange layer did not hinder entirely Li-ion transport through the separator. In addition, the microstructures of the separators were reconstructed based on focused ion beam/scanning electron microscopy tomography to determine the effective ionic conductivity and effective tortuosity of the PP-*g*-PLiSS separators. These values showed that ion mobility within the separator changed with increasing graft level, indicating that the concentration of SS groups and bulk porosity of the separator have to be adjusted to maintain the effective conductivity at a practical level.

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1. Introduction

Despite a decade of intense research on lithium–sulfur (Li–S) batteries, commonly considered as a successor to current Li-ion battery technology, the chemistry of this system remains challenging. Apart from the difficulties associated with using Li metal [1], the "holy grail" of negative electrodes for rechargeable batteries [2,3], the positive electrode based on sulfur also contributes substantially to defining the stability and performance of Li–S batteries, especially for long-term operation. This is mainly due to the complex mechanism by which S_8 is reduced to Li_2S, along with the formation and dissolution of Li polysulfides, Li_2S_n ($n = 2$, 3, 4 . . . 8), which constitute the active material of Li–S batteries, but also a major source of problems. As polysulfides are highly soluble in organic liquid electrolytes, these species can readily diffuse through the separator to the negative electrode [4,5]. There, polysulfides chemically react with Li metal (the "state-of-the-art" negative electrode for Li–S batteries), are reduced to shorter S_n^{2-} chains, and diffuse back to the positive electrode. This back and forth diffusion accompanied by redox reactions constitutes the so-called "polysulfide redox shuttle" [4,6], which, in turn, significantly reduces the coulombic efficiency of the cell and may even lead to an "infinite" charge [4].

Although important advances have been made in recent years to confine polysulfides within the positive electrode (e.g., by

confining sulfur in various conductive porous carbon matrices [7–16]), to prevent the reaction of polysulfides with the Li metal electrode (e.g., by using $LiNO_3$ as an electrolyte additive [17–19]), and to control or reduce the dissolution of Li_2S_n species in the electrolyte (e.g., by using (partially) fluorinated ether-based electrolytes [20–23]), the polysulfide shuttle continues to limit the progress of Li–S batteries. Most of the proposed solutions only partially retain harmful Li_2S_n species at and near the positive electrode or partially control the dissolution of polysulfides in the electrolyte, and their function is often limited over time [24]. Recently, components other than the positive electrode and electrolyte have also been investigated as shuttle-retardants. One example is the separator, thus far mostly considered as a passive component of the cell. By adding adequate functionality (surface and/or bulk) to a classical polypropylene (PP) separator, the limitations of Li–S batteries, in particular the polysulfide redox shuttle [25–28], can be addressed. Moreover, the utilization of sulfur can be maximized, especially for sulfur that is normally mostly inactive owing to precipitation in the pores of the separator [29] or on the surface of Li, and, thereby, the overall performance of the battery can be significantly enhanced. There have been four main strategies reported in the literature for separator functionalization, namely deposition of carbon [30–33], oxide [34,35], polymer [25–27,36,37] and multi-component coatings [38–40] on the separator. Although these studies showed promising electrochemical results, the impact of separator modification has been rarely investigated in detail [38–40] and, therefore, the influence of separator chemistry on the electrode/electrolyte interfacial resistance as well as the transport properties of the separator and other cell components still needs deeper studies to provide unambiguous interpretation.

Herein, we complement the electrochemical impedance spectroscopy (EIS) experiments on symmetric cells described in Part 1 of this study [41] by investigating the transport properties of asymmetric polypropylene-*graft*-poly(lithium styrene sulfonate) (PP-*g*-PLiSS) separators with polysulfide barrier properties and Li^+ exchange sites, which have been developed and studied as an alternative to Celgard, the state-of-the-art separator for Li–S batteries [42,43]. Introduction of one-sided functionality, here a cation-exchange layer, onto a separator carries the risk of generating a new interface and, thus, adding a new resistance to the electrochemical cell, which is already resistance-laden. Through the analysis of symmetric Li/Li cells with PP-*g*-PLiSS separators with increasing concentrations of cation-exchange groups, we determined when this new interface develops and, more importantly, how detrimental it is to the entire cell. In particular, we focused on the influence of the cation-exchange layer on Li electrode/electrolyte interfacial properties and on effective conductivity through the separator (as a change in electrolyte resistance).

2. Experimental

2.1. Cell assembly

EIS measurements were carried out using a standard coin-type cell, in which the separator was placed between two identical Li metal electrodes (thickness = 0.75 mm, ø = 13 mm, Alfa Aesar). Two classes of separators were studied, namely polypropylene-*graft*-poly(sodium styrene sulfonate) (PP-*g*-PNaSS), the end-product of the graft copolymerization reaction [42], and its Li-substituted counterpart PP-*g*-PLiSS. PP-*g*-PNaSS, which had a 30% graft level (GL), was investigated to assess the impact of Na counterions on the Li electrode/electrolyte interface. PP-*g*-PLiSS separators with two distinct graft levels (GLs) (8% and 30%) were chosen as

representative asymmetric separators with low and high concentrations of cation-exchange groups, respectively. The transport properties of PP-*g*-PLiSS separators with other GLs were also investigated. However, for simplicity, we will refer to these results only when calculating the effective conductivity and effective tortuosity of the separator.

Prior to cell assembly, each grafted separator was presoaked in the electrolyte, 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) in a mixture of dimethoxyethane (DME) and 1,3-dioxolane (Diox) (2:1 by weight, BASF), to ensure complete wetting. Once placed in the cell, 30 μL of electrolyte was added for complete wetting of the other cell components. PP TreoPore (thickness = 25 ± 5 μm, pore size = 0.05 μm, TreoPore, also referred to as PP base polymer) and Celgard 2400 (thickness = 25 μm, pore size = 0.04 μm, Celgard®, USA), used as reference separators, were not presoaked in the electrolyte. Instead, they were directly wetted with 50 μL of electrolyte during cell assembly.

2.2. Separator thickness and electrolyte conductivity

The thicknesses of PP TreoPore and its grafted derivatives were determined using a digital thickness gauge (MT1281, Heidenhain). The conductivity of the electrolyte, $\sigma_0 = 13.1$ mS/cm, was measured at room temperature with a conductivity meter (WTW Weinheim) equipped with a graphite electrode (TetraCon® 325).

2.3. Electrochemical impedance spectroscopy

EIS measurements were performed as described in our previous publication [41]. Briefly, a sinusoidal perturbation of 10 mV was applied to the symmetric Li/Li cell under open circuit conditions in the frequency range of 1 MHz to 50 mHz. The impedance of each cell was measured repeatedly (100 times) every 5 min. The resistance values were normalized to the geometrical area of the electrode (1.3 cm^2).

2.4. Poly(styrene sulfonate)-containing electrolyte

To mimic the possible dissolution of poly(styrene sulfonate) (PSS) grafts from the PP-*g*-PLiSS separatorand their interactions with polysulfides present in the electrolyte, PSS was added to either the standard electrolyte or an electrolyte containing Li_2S_6 (prepared as described in Part 1 of this study [41]). Because the Li-form of PSS (PLiSS) is not available commercially, we used its Na^+-counterpart (PNaSS, Alfa Aesar, $M_W \sim 300,000$). The amount of PNaSS added to the standard electrolyte or that containing Li_2S_6 was equal to the mass of the PSS graft component in the highly grafted separator (20 mg/mL).

2.5. Ion-exchange capacity

The ion-exchange capacity (IEC) of the asymmetrically functionalized separators with 8% and 30% GLs was determined through acid–base titration. To determine the IEC, the PP-*g*-PNaSS separator was first converted to the H^+-form (PP-*g*-PSSA) by immersion in 2 M H_2SO_4 overnight. The $Na^+ \rightarrow H^+$ ion-exchange step was followed by multi-solvent exchange and evaporation treatment [44], which was carried out for a shorter time (1 h) than described previously [42] to minimize the possible dissolution of PSS chains from the grafted separator. Any residual solvent was evaporated under vacuum at 60 °C for 24 h. Next, discs with a 20 mm diameter were punched out of the PP-*g*-PSSA sample and immersed overnight in 1 M KCl solution. The solution was then titrated with 0.05 M KOH using SM Titrino 702 titrator (Metrohm). Subsequently, the PP-*g*-PSSA discs were subjected to multi-solvent exchange and evaporation to preserve the asymmetry [42], dried