Communication—Lithium Sulfonated Polyoxadiazole as a Novel Single-Ion Polymer Electrolyte in Lithium-Ion Batteries

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A single-ion conductor polymer electrolyte was prepared and the effects of the ratio of isophthalic acid (IPA) to 4, 4’-diphenyl ether dicarboxylic acid (DPE) on the structure and electrochemical properties have been investigated. Results show that all the lithium sulfonated polyoxadiazoles (Li-SPODs) have excellent thermal stability (510 °C). The ionic conductivity of the Li-SPOD is 7.2 × 10⁻⁴ S cm⁻¹ at room temperature when the IPA/DPE ratio is 6/4. A high Coulombic efficiency of 99.1% for the LiFePO4/6/4 Li-SPOD SPEs/Li half-cell could be achieved with a capacity retention of 90.63% at a current density of 0.1 C after 25 cycles. © 2020 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/1945-7111/ab6e5c]
of O=S=O, respectively. The peak at 1032 cm\(^{-1}\) ascribes to the stretching vibration of S-O. The peak of 1602 cm\(^{-1}\) is the stretching vibration of C=N on the oxadiazole ring.\(^{15}\) The presence of the characteristic peaks above indicates that the structure of sulfonated polyoxadiazole with sulfonate groups can be obtained by the reaction conditions used in this study.\(^{16}\)

Figure 1b shows the XRD patterns of Li-SPOD polymers. Two broad diffraction peaks at around 8° and 25° appear in the range of 5° \(\sim\) 40° for all three samples. With the increase of DPE monomer content, the 25° diffraction peak slightly offset to the direction of low angles. According to the Bragg formula,\(^{17}\) the crystalline interplanar spacing of the polymer increases, but the crystal structure has not changed. At the same time, the higher the content of the DPE monomer is, the greater intensity of the diffraction peak is, because the DPE monomer can provide more ether bonds, which can improve the flexibility of the polymer chain and make it easier to crystallize.

TGA tests were carried out to characterize the thermal stability of Li-SPOD polymers. Figures 1c and 1d show the TG curves and DTG curves of Li-SPOD polymers, respectively. The mass of Li-SPOD polymers has a small loss before 200 °C, which indicates the combined water loss in the polymer. With the increase of DPE content and the sulfonation degree, the mass loss becomes greater. When the temperature increases to 477 \(\sim\) 484 °C, the Li-SPOD polymers are decomposed rapidly due to the removal of \(-\text{SO}_3\text{Li}\) and the degradation of the polymer chain. The maximum thermal

![Scheme 1. Schematic diagram of the chemical reaction of Li-SPOD preparation.](image)

![Figure 1. The structure and thermal properties of Li-SPOD polymers: (a) ATR-FTIR spectra, (b) XRD patterns, (c) TGA curves, and (d) DTG curves.](image)
decomposition temperature of the Li-SPOD polymers is 510 °C, and the carbon residue is above 50 wt% at 800 °C. The above results demonstrate that Li-SPOD polymers have excellent thermal stability. The results of the thermal stability of Li-SPOD polymers are summarized in Table SI (see Supporting Information). The T5% of the polymers decreases gradually with the increase of DPE content, which may be influenced by the steric hindrance effect of –SO3Li.18

The Nyquist plots of the electrochemical impedance for Li-SPOD SPEs in different temperatures are displayed in Fig. 2. The AC impedance spectra of the Li-SPOD SPEs are straight lines, which indicate that the samples have good contact and do not react with the stainless steel electrode.19 Meantime, the bulk resistance of the Li-SPOD SPEs decreases gradually with the increase of temperature. The detailed values of ionic conductivity at different temperatures were calculated, as shown in Table I. The ionic-conductivities of all the Li-SPOD SPEs at room temperature reaches 10^(-4) ~ 10^(-3) and increase with the increment of sulfonation degree at the same temperature, which are higher than those of most reported SPEs20–26 (see Table SII in Supporting Information). Moreover, with the increase of DPE content, the lithium-ion transference number of the Li-SPOD SPEs increases (as shown in Fig. S1 and Table III of supporting information). The Tli+ of SPEs are 0.68-0.82, which exhibits the single-ion conducting behavior.

The Arrhenius plots for the ionic conductivities of the Li-SPOD SPEs are presented in Fig. S2. It indicates that the lg σ of the Li-SPOD SPEs have a linear relationship with the inverse of temperature (1/T), conforming to the Arrhenius equation. The ionic conduction activation energy of Li-SPOD SPEs is obtained by fitting the straight line, as shown in Table I. The values of Ea are all about 17 kJ mol⁻¹, which is comparable to that of most sulfonate-based SPEs.

The electrochemical window is also an important parameter of electrolyte performance, which determines the using range of the electrolytes. The CV curves of Li-SPOD SPEs are shown in Fig. 3. There is no significant difference in CV curves of Li-SPOD SPEs, showing a similar redox reaction, which indicates that the copolymerization ratio has little effects on the electrochemical window of the SPEs. A reduction reaction occurs from about −0.3 V at the working electrode, indicating that Li⁺ in the SPEs obtain electrons and deposits them on the surface of the working electrode. At about 0.5 V, an oxidation reaction occurs on the working electrode, corresponding to the lithium depositing on the working electrode loses electrons and returning to the Li-SPOD SPEs. The above two processes prove that after being swollen by DMSO, Li-SPOD SPEs can achieve the Li⁺ reversible redox reaction process and be used as an SPE membrane. When the voltage reaches 4 V, the Li-SPOD SPEs begins to decompose. In other words, the electrochemical window of Li-SPOD SPEs is 4 V (vs Li/Li⁺). Besides, as shown in the supporting information in Fig. S3, when the half cell was run in the range of −1.5 ~ 2 V, only the redox peak of lithium deposition and removal on the working electrode could be observed. However, when the half-cell was run in the range of 1 ~ 4.5 V, an obvious reduction peak appears near 1.3 V is observed, and a relatively gentle oxidation peak appeared in the range of 1.5 ~ 2.5 V. These reversible REDOX peaks ascribe to the doping and undoping process of SPE because POD is a kind of conjunctive polymer, which could be n-doped in a reductive environment. The SPE was prepared by copolymerized POD with diphenyl ether structure, so the n-doped SPE is still electronic insulating and can work as an SPE.

The specific capacity of discharge and Coulombic efficiency of Li-SPOD SPEs half cells under 0.1 C are shown in Fig. 4. The inserted pictures are the first charge-discharge curves of the half cells, which indicates that the Coulombic efficiency of the cell with 8/2 Li-SPOD, 7/3 Li-SPOD, and 6/4 Li-SPOD are 98.1%, 98.0%, and 99.1%, respectively. With the increase of cycle numbers, the specific discharge capacity of the cell with Li-SPOD SPEs decreases gradually, in which the 8/2 Li-SPOD SPEs decreases most significantly, from 141.4 to 119.6 mAh g⁻¹ after 25 cycles. The Coulombic efficiency changes little, indicating that the active electrode material may be consumed due to the reaction between the electrolyte during the charging and discharging cycle, or the integrity of the electrode may be gradually destroyed during the cycle leading some active materials cannot participate in the reaction.27 After 25 cycles of the cell with 7/3 Li-SPOD SPEs, the capacity decreases from the highest 145 to 128.2 mAh g⁻¹, and the Coulombic efficiency also decreases slightly in the cycle process, which indicates that the electrolyte might decompose slightly in the charge-discharge process. The capacity of 6/4 Li-SPOD SPEs falls to 132.6 from 146.3 mAh g⁻¹ after 25 cycles and Coulombic efficiency slightly lower. When the current density increases to 0.5 C or 1 C, the conductivity is too small to transfer Li⁺ in time, as well as the side reactions of electrolyte increase. Hence the capacity of the battery decreases significantly, and the rate performance is poor (see Fig. S4 in Supporting Information). As shown in results, with the increment of DPE content, the ionic conductivity increases gradually, contributing to the improvement of SPEs cycle stability.

| Table I. Conductivity of Li-SPOD SPEs swelled by DMSO at different temperatures. |
|-----------------|----------|----------|----------|----------|----------|----------|-----------------|
| Samples         | 25 °C    | 40 °C    | 50 °C    | 60 °C    | 70 °C    | Activation energy (kJ mol⁻¹) |
| 8/2 Li-SPOD     | 0.42     | 0.57     | 0.74     | 0.91     | 1.09     | 17.76                                      |
| 7/3 Li-SPOD     | 0.55     | 0.75     | 0.93     | 1.15     | 1.34     | 16.68                                      |
| 6/4 Li-SPOD     | 0.72     | 0.97     | 1.172    | 1.58     | 1.78     | 17.13                                      |
Lithium sulfonated polyoxadiazoles with different degrees of sulfonation were synthesized and used as gel polymer electrolytes in LIBs. The ATR spectrum proved that the sulfonic acid group was successfully grafted into SPOD. The TG test showed that the polymers have good thermal stability, and the initial thermal decomposition temperature decreases slightly with the increase of DPE monomer content. The conductivity of SPOD SPEs is \( \sim 10^{-4} \text{ S cm}^{-1} \) at room temperature, which is at a high level in polyanionic solid electrolytes. However, the electrochemical window of Li-SPOD is narrow. The 6/4 Li-SPOD SPEs have a good cycle performance, and the Coulombic efficiency is always maintained at a high level. Although its basic research has made great progress, the application is still in the initial stage, and further research is needed.

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