

All-solid-state secondary lithium battery using solid polymer electrolyte and anthraquinone cathode



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ABSTRACT

An all-solid-state battery was fabricated by using a PEO-base solid polymer as electrolyte and an organic material anthraquinone (AQ) as cathode. The anthraquinone delivers a specific discharge capacity of 183 mAh g⁻¹ at first cycle at current density of 20 mA g⁻¹ at 65 °C. The use of solid polymer electrolyte reduces the dissolution of organic active material greatly, improving the cycle performance of the battery. Therefore, the all-solid-state battery delivers a better cycling property. It can still retain a capacity of 136 mAh g⁻¹ after 50 cycles, corresponding to a capacity retention of 74%, while capacity retention of the cell using liquid electrolyte was only 28% after 20 cycles. The all-solid-state battery shows more stable interfacial resistance during charge–discharge process. It displays good rate ability and a better thermal stability.

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1. Introduction

Rechargeable Li-batteries are currently essential power sources due to their numerous valuable applications as power storage for portable electronic devices and emerging large-scale applications [1]. However, commonly used cathode materials such as LiCoO₂, LiFePO₄ are inorganic materials, are facing serious problems relating to safety and resource costs. Over the past few years, organic electrodes have emerged as a promising cathode material because of their beneficial properties. They are potentially environmental friendly, cheap, abundant and recyclable materials, and can be made from biomass via ecofriendly processes with minimum energy consumption [2–6]. Furthermore, they can be designed with higher capacities and their electronic properties can be tuned by changing their structure and substituents [7,8]. However, organic materials always exhibit poor cyclability because they suffer from severe dissolution in liquid organic electrolyte. During the past few years, a lot of ways have been tried to overcome this issue, such as optimization of molecular structure, covalent attachment of redox molecules to substrates, and polymerization of organic materials [8–14]. All those ways were effective to some extent, but the dissolution problem has never been resolved fundamentally. Solubility in liquid electrolyte is still one of the biggest problems of the organic materials. Hence new strategy other than modification to the materials should be proposed to inhibit dissolution. Replacing traditional liquid

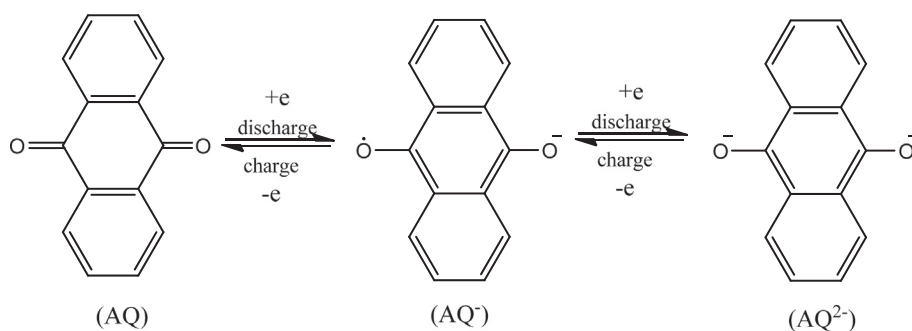
electrolyte with solid-state electrolyte will be an effective way to solve the problem.

Lithium based solid polymer electrolytes consist of polymer matrix and lithium salt. SPE based on PEO shows a high electrochemical stability and has been researched for a lot of years. The ionic conductivity of SPEs at room temperature isn't high enough when compared with liquid electrolytes and is always improved by adding plasticizers or inorganic ceramic fillers to increase their amorphous phase of the polymer matrix. Compared with conventional liquid electrolytes, solid polymer electrolyte (SPE) has lots of advantages such as favorable mechanical properties, ease of fabrication into thin films, formation of a stable interface with Li metal, and prevention of Li dendrite formation if the modulus of the polymer is high enough [15,16]. All-solid-state batteries based on solid polymer electrolytes possess not only better cycle life but also great flexibility, enabling design and manufacture of wearable or other new kinds of energy storage devices and electric vehicles [17]. In the meantime, solid electrolyte has superior performance in safety aspects than in liquid organic electrolyte [18]. PEO-based solid polymer electrolyte was reported in 1973, and has been used in many aspects, such as inorganic materials, solar cells, and lithium-sulfur batteries, and achieved excellent performance [19,20]. However, all-solid batteries using organic cathode materials and solid polymer electrolyte have been seldom reported. And few polymer electrolyte and cathode material has been investigated.

Herein we report an all-solid-state lithium organic battery consisting of a PEO-based solid polymer electrolyte (SPE) and an organic cathode material, anthraquinone (AQ), which includes the redox process of the quinonyl group (Scheme 1). The electrochemical performance of the

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Scheme 1. Redox mechanism of AQ.

all-solid-state battery was characterized, including charge–discharge profile, cycling property, rate capability, etc. The thermal stability of anthraquinone with polymer electrolyte was also studied compared with the liquid electrolyte.

2. Experimental section

2.1. Preparation of solid polymer electrolyte

The polymer electrolyte was obtained by a modification of the hot-pressing technique according to literature [21]. PEG and LiTFSI were first weighed and mixed in a mortar. Then PEO and γ -LiAlO₂ were slowly added. The formed homogenous rubber-like mixture was then placed between two Mylar sheets, followed by pressing at about 1000 N cm⁻² for 10 min at 100 °C, and then slowly cooled to room temperature. A mechanically stable membrane with an average thickness of 150 μ m was obtained.

2.2. Electrode preparation and cell assembly

The composite cathode was also prepared by a dry, solvent-free procedure. PEG (Aldrich, average MW = 2000) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Aldrich, 99%), were weighed to give an EO/Li ratio of 20 (EO = ethylene oxide unit) and mixed in a mortar. Anthraquinone and Super-P were dried at 100 °C in a vacuum oven overnight and then gently mixed. Then the two blends were mixed together and homogenized in the mortar. The component weight percentage of the composite cathode was 35% AQ, 25% Super-P, 10% LiTFSI and 30% PEG. The electrode was obtained by screen printing the composite cathode on the aluminum sheet heated at 80 °C.

Cells were assembled by sandwiching a polymer electrolyte disk between a lithium foil and the composite cathode. The diameter of the cathode was 1.2 cm and the mass loading was about 4 mg. The cells were assembled in glove box filled with argon gas.

2.3. Characterization and measurements

The ionic conductivity of the polymer electrolyte was obtained by testing the impedance of the SS/AQ/SS battery. The battery was assembled by sandwiching the polymer electrolyte film between two stainless steel (SS) electrodes. The ionic conductivity of the polymer electrolyte, σ was calculated using the following equation:

$$\sigma = \frac{L}{R_b S}$$

where L is the thickness of the film, R_b is the bulk resistance and S is the area of electrolyte–electrode contact.

Electrode properties were evaluated using CR2016 coin-type cells. The cyclic voltammograms (CV) were performed on a workstation (AMTECT Company). The charge–discharge experiments were carried

out on a LAND CT2001A Battery Cycler (Wuhan, China). The specific capacity was calculated on the basis of the amount of the active material. The electrochemical impedance spectroscopy (EIS) was got on the work station (Princeton Applied Research, AMTECT Company). The frequency limits were set at 10⁵–10⁻¹ Hz with an AC oscillation of 5 mV. All the solid state cells were tested at 65 °C unless noted.

Electrode materials for differential scanning calorimetry (DSC) measurements were carried as follows. The charged-state cathode materials and electrolyte were hermetically sealed in gold-plated copper stainless steel capsules in the glove-box. The DSC scans were performed using a DSC 200F3 instrument (NETZSCH, Germany) with a scanning rate of 10 °C/min. The weights of DSC pans were measured before and after the DSC measurements to ensure no leakage occurred during the experiments [22].

3. Results and discussion

In order to employ the polymer electrolyte into all-solid-state batteries, the ionic conductivity of the SPE was examined. By testing the electrochemical impedance spectroscopy (EIS) of solid polymer electrolyte tested at different temperatures, the ion conductivities at different temperature from 25 to 65 °C are obtained. The ionic conductivity of the solid polymer electrolyte at different temperatures was summarized in Table 1. The ionic conductivity of the polymer electrolyte increases with the temperature, which agrees well with other works [23,24]. The temperature dependence of the ionic conductivity for the solid polymer electrolyte is shown in Fig. 1. The curve suggests that the conductivity follows Arrhenius equation, $\sigma = \sigma_0 \exp(-E_a/RT)$, where σ_0 is the pre-exponential factor, E_a is the activation energy, R is the gas constant, T is the testing temperature in Kelvin scale. The E_a is 0.09 eV. The ionic conductivity reaches 8.21 $\times 10^{-4}$ S cm⁻¹ at 65 °C, which is a little bit lower than the liquid electrolyte, but it is a satisfactory value for their future application in lithium-ion batteries.

The electrochemical performance of all-solid-state Li/SPE/AQ battery was investigated systematically. Fig. 2 shows charge–discharge profile and cyclic voltammetry curve of AQ in polymer electrolyte and traditional liquid electrolyte. CV was carried out by scanning the potential between 1.5 and 3.5 V at a scan rate of 0.1 mV s⁻¹ (Fig. 2a). The CV curve shows one pair of symmetric redox peaks near at 2.3 V. For comparison, AQ was also tested in 1 M LiTFSI/DOL + DME liquid electrolyte. The CV curve also shows a pair of redox peaks centering at 2.33 V with

Table 1
Ion conductivity of solid polymer electrolyte.

Temperature/°C	Ion conductivity/S cm ⁻¹
25	7.10 $\times 10^{-5}$
35	1.61 $\times 10^{-4}$
45	2.73 $\times 10^{-4}$
55	4.64 $\times 10^{-4}$
65	8.21 $\times 10^{-4}$

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