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Separator for lithium-sulfur battery based on polymer blend membrane

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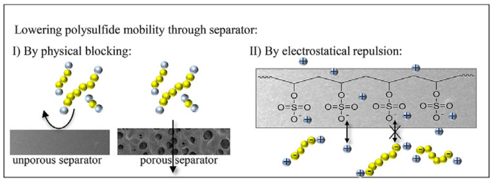
HIGHLIGHTS

- Polyvinylsulfate potassium salt is used as membrane additive in the Li-S battery.
- Polysulfide mobility is reduced resulting in highly increased cycling stability.
- The negative effect of membrane porosity in the lithium-sulfur test is shown.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work we report a novel way of reducing the polysulfide shuttle in lithium-sulfur batteries by a new separator material. Polyvinylsulfate potassium salt (PVSK) as polymeric additive is introduced into a polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) matrix membrane to improve the battery performance. PVSK is expected to lower the polysulfide mobility due to interaction with the sulfonic group. PVdF-HFP/PVSK blend membranes are prepared and an UV/Vis polysulfide diffusion test clearly demonstrates the positive effect of PVSK. Electrochemical testing reveals a significant improvement of cycling stability up to more than 200 cycles. In addition, the effect of separator porosity to the polysulfide shuttle is investigated with PVdF-HFP membranes of different porosity. A simple polysulfide diffusion test and potentiostatic charge/discharge cycling clearly demonstrate that low separator porosity is favorable in a lithium-sulfur cell.

1. Introduction

One of the most urgent challenges in efficient use of alternative energy sources is the improvement of energy storage devices. For example, estimations predicts an increase of energy produced by wind power by a half (43–61 PWh per year) and energy produced by solar-photovoltaics by four-times (939–4105 PWh per year) from year 2000–2050 [1]. The most important requirements are complete storing of energy and usage at any time, for user demands. In addition, the energy must be stored not only in the stationary batteries. For example there is strong trend in increasing wish for affordable electrical driven cars. It is estimated that by 2050 the number of cars and trucks in use will doubled (1.2 to over 2.5 billion) [2]. This high increase makes the improvement of energy storage devices an even more pressuring task, to reach electrical power ideally for all vehicles.

Among energy storage devices the lithium-sulfur cell is one of

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the most promising candidates for becoming the battery system of near future. Its theoretical gravimetric energy density of 2500 Wh kg-1 is over four times higher than the ideal state of common lithium-ion batteries (LIB) [3]. The theoretical capacity of 1675 mAh g_S-1 is up to seven times higher than that of LIBs [4]. In addition, the Li–S system is of lower cost, reduced volume and weight and more environmental friendly [5,6].

Although the first systems were already tested in the 1960s [7], severe drawbacks still limit the cell performance achieved. The reaction between lithium and sulfur leads to conversion of up to sixteen electrons per sulfur molecule (S_8), resulting in the high theoretical capacity [8–10]. During discharge, polysulfides ($Li^+S_x^{2-}Li^+$) of different length are formed. Although their formation is necessary to achieve the high energy output, they cause several problems. Due to their solubility in liquid electrolytes commonly used in Li–S systems, the polysulfides leak out of the cathode structure. This can lead to severe loss of active material in the cathode and passivation layers of less soluble polysulfide species can build up on the electrodes [11,12].

Several approaches have been pursued to overcome the problems, typically improving single components of the battery cell, with main focus on cathode research. A cell component with high promise is the separator membrane. Commercial separators are mostly porous polyolefin materials. However, for the special case of the lithium-sulfur cell, they do not repel or impede the polysulfides, but even allow high polysulfide mobility due to high porosity instead. For example, one can use coatings between commercial separators and the cathode, like carboneous coatings. The material shall reduce the mobility of polysulfides by introducing an additional, porous, even electrically conductive layer. Zhang et al., for example, used porous hollow carbon, which provides chemical and physical adsorption of polysulfide species through nitrogen-doping [13]. Wei et al. and Zhang et al. created a layer of the carbon material Super P and PVdF (polyvinylidene fluoride) onto Celgard [14,15]. This leads to a more hydrophilic surface with better adsorption of the hydrophilic polysulfides. Tested cells showed a lower difference of charge and discharge voltage due to better reaction kinetics with the modified film. Graphene oxide layers may enhance the cell performance due to carboxylic groups, which allow Li^+- ion hopping, but restrict S_x^{2-} mobility [16]. The layer thickness on Celgard is typically around 5–20 µm.

Another coating approach uses the ion-conductive material Nafion [17–21]. Its highly fluorinated chemical structure (Fig. 1) offers negatively charged sulfonic groups in its sidechain. This functionalization is expected to provide repulsion of negatively charged polysulfide anions S_x^{2-} by electrostatic interaction, whereas hopping of lithium cations is allowed [20]. Enhanced cycling performance is shown e. g. by Jin et al. using a purchased Nafion film [18] or by Bauer et al. and Huang et al. using Nafion-coated Celgard membrane as separators [20,21].

The presented carboneous and Nafion coatings have improved the battery performance due to their chemical (attractive interactions, functional groups) and their structural properties (porosity). However, material research in that direction is at its infancy. Frequently, the materials under test are chosen based on materials tested in other battery systems, without following a systematic approach. For example, the relatively complex structure of Nafion leads to the question, if polymer materials of simpler structure containing sulfonic groups can have similar effects as well. In addition, most studies on separator modifications ignore the porosity effect. When a porous membrane is coated with a dense layer (like Nafion), the polysulfide mobility might be already reduced due to lower porosity compared to the uncoated separator. Within this study, we have tried to undertake a systematic approach. Instead of Nafion the polymer polyvinylsulfate potassium salt (PVSK, Fig. 1) is tested as polymeric separator additive. Its sulfonic group is expected to have the same positive effects as the one in the Nafion structure, but the polymer is of more simple chemical structure. This shall also clarify if the positive effect of Nafion coating is based on the interaction with sulfonic groups. In addition, the influence of the separator porosity is investigated.

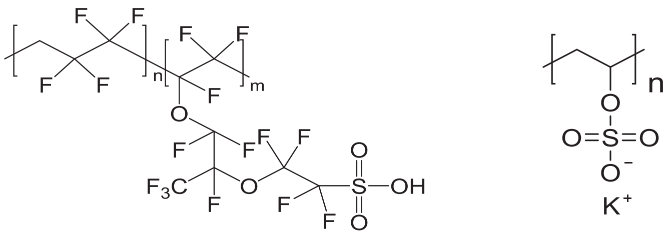

Fig. 1. Chemical structure of Nafion (left) and polyvinylsulfate potassium salt (right).

2. Experimental

2.1. Preparation of blend membranes

For implementation to industry easy material preparation methods are needed. The tested material was produced via simple blend membrane preparation, which is the easiest process to develop polymer membranes. PVdF-HFP/PVSK blend membranes with PVSK content of 5, 10 and 20 wt% have been prepared. For the comparison membrane, which consists of pure PVdF-HFP (polyvinylidene fluoride-hexafluoropropylene, statistical copolymer, Sigma Aldrich 427160), 0.5 g of the polymer were dissolved in 10 mL dimethyl sulfoxide (DMSO). The blend membranes were prepared by substituting part of the PVdF-HFP with PVSK (Sigma-Aldrich 271969). For a resulting mass of 5 wt% PVSK 0.475 PVdF-HFP and 0.025 g PVSK are dissolved in separate vials in 7 and 3 mL DMSO (10 wt%: 0.45 + 0.05, 20 wt% 0.40 + 0.10 g). When both polymers were completely dissolved after two days, the PVdF-HFP solution was added to the PVSK solution. After stirring overnight, the resulting solution was casted onto a 10 × 10 cm stainless-steel form on aluminium foil. The casted membrane was dried in the oven at 60 °C under vacuum overnight. Freestanding membranes of around 30 µm thickness were obtained.

2.2. Preparation of PVdF-HFP membranes of different porosity

A different approach of sample preparation had to be chosen to create samples for testing the influence of separator porosity on the polysulfide flow. For preparation of stable PVdF-HFP membranes of different porosity and homogeneous thickness, one Celgard2325 layer (22 µm thickness, P = 39%) had to act as matrix material. The membranes were formed via phase-inversion process analogous to Jeong et al. [22], using acetone as solvent and water as non-solvent. For the non-porous, solid membrane, 0.12 g PVdF-HFP were dissolved in 3 mL acetone. For the porous membranes water in a specific weight ratio (X wt%) was added. 0.12 g PVdF-HFP were dissolved in acetone volume $V_{acetone} = 3$ mL - X (values for mass and volume see **suppl. Mat. S1**). Membranes using 2, 4 and 6 wt% water addition can be casted as stable membranes, with higher water amount the polymer solution was to viscous **(S2)**.

The mass/volume of water (m_{H2O}) was calculated according to equation (1).