



ELSEVIER

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

In-situ covalent bonding of polysulfides with electrode binders in operando for lithium–sulfur batteries

ChangAn Yang^a, QiaoKun Du^b, Zeheng Li^b, Min Ling^{b,*}, Xiangyun Song^c, Vincent Battaglia^c, Xiaobo Chen^d, Gao Liu^{c,**}

^a Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414006, Hunan Province, PR China

^b Zhejiang Provincial Key Laboratory of Advanced Chemical Engineering Manufacture Technology, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China

^c Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA

^d Department of Chemistry, University of Missouri – Kansas City, Kansas City, MO, 64110, USA

HIGHLIGHTS

- Shuttling polysulfide be captured by our binder via a nucleophilic substitution reaction.
- The activity of primary alkyl chloride is much higher than secondary alkyl chloride.
- The sequence of the absorption ability of binders with polysulfides is PECH > PVC > PVDF.
- Cycling under high sulfur mass loading with high areal capacity.

ARTICLE INFO

Keywords:

Energy storage
Lithium sulfur battery
Polymer binder
Nucleophilic substitution
Polysulfides

ABSTRACT

Dissolved polysulfides cause high self-discharge, low coulombic efficiency and short cycling life due to their shuttle effect in the charge/discharge cycles in lithium-sulfur (Li-S) batteries. Despite of various attempts (e.g., addition of metal oxides and chalcogenides in the cathode, immobilization of sulfur with various carbons, and confinement of sulfur within the cathode side with membranes) in solving this problem, it still remains a major challenge for Li-S batteries. Here, we demonstrate that chemically active binders can in situ bond to the polysulfides in the electrode. Besides the common binding functions of the cathode materials to the current collector, the covalent bonding between binders and polysulfides could bestow the higher capacity, stable cycling and high coulombic efficiency, even under the high loading of sulfur contents. Thus, this study provides an alternative and effective way in solving the shuttle effect of the dissolved lithium polysulfides for Li-S batteries.

1. Introduction

With the blooming market of portable electronic devices, commercialized lithium ion batteries are considered insufficient to meet the blooming market of energy storage systems. In this regard, Lithium-sulfur (Li-S) batteries, show great potential for the next generation of lithium-ion batteries due to its high theoretical specific capacity of 1675 mA h g^{-1} and energy density of 2600 W h kg^{-1} . Additionally, the elemental sulfur is low-cost, nontoxic, and abundant. Nevertheless, one of the main obstacles that hinder the progress of Li-S batteries is the shuttle effect caused by electrolyte soluble long-chain polysulfides, which is the lithiated product of sulfur. The shuttle effect of the

dissolved lithium polysulfides has causes a high self-discharge loss, a low coulombic efficiency, and a short cycling life for Li-S batteries. Thus, one of the straightforward and promising solutions is to fix the polysulfides to the cathode matrix by either chemical bonding or physical confinement. For example, metal oxides and chalcogenides have been introduced into the electrode for their strong binding of polysulfides, resulting in considerable gains in coulombic efficiency and cycling stability [1–8]. Immobilization of sulfur seems to be another promising approach with various carbon materials such as carbon paper [9,10], carbon nanotubes [11,12], porous carbon [13–15], graphene [16], etc. Solid-state membranes have also been attempted to eliminate the shuttle effect by confining the polysulfides within the cathode side

* Corresponding author.

** Corresponding author.

E-mail addresses: minling@zju.edu.cn (M. Ling), gliu@lbl.gov (G. Liu).

<https://doi.org/10.1016/j.jpowsour.2018.09.008>

Received 17 May 2018; Received in revised form 5 August 2018; Accepted 3 September 2018

0378-7753/© 2018 Elsevier B.V. All rights reserved.

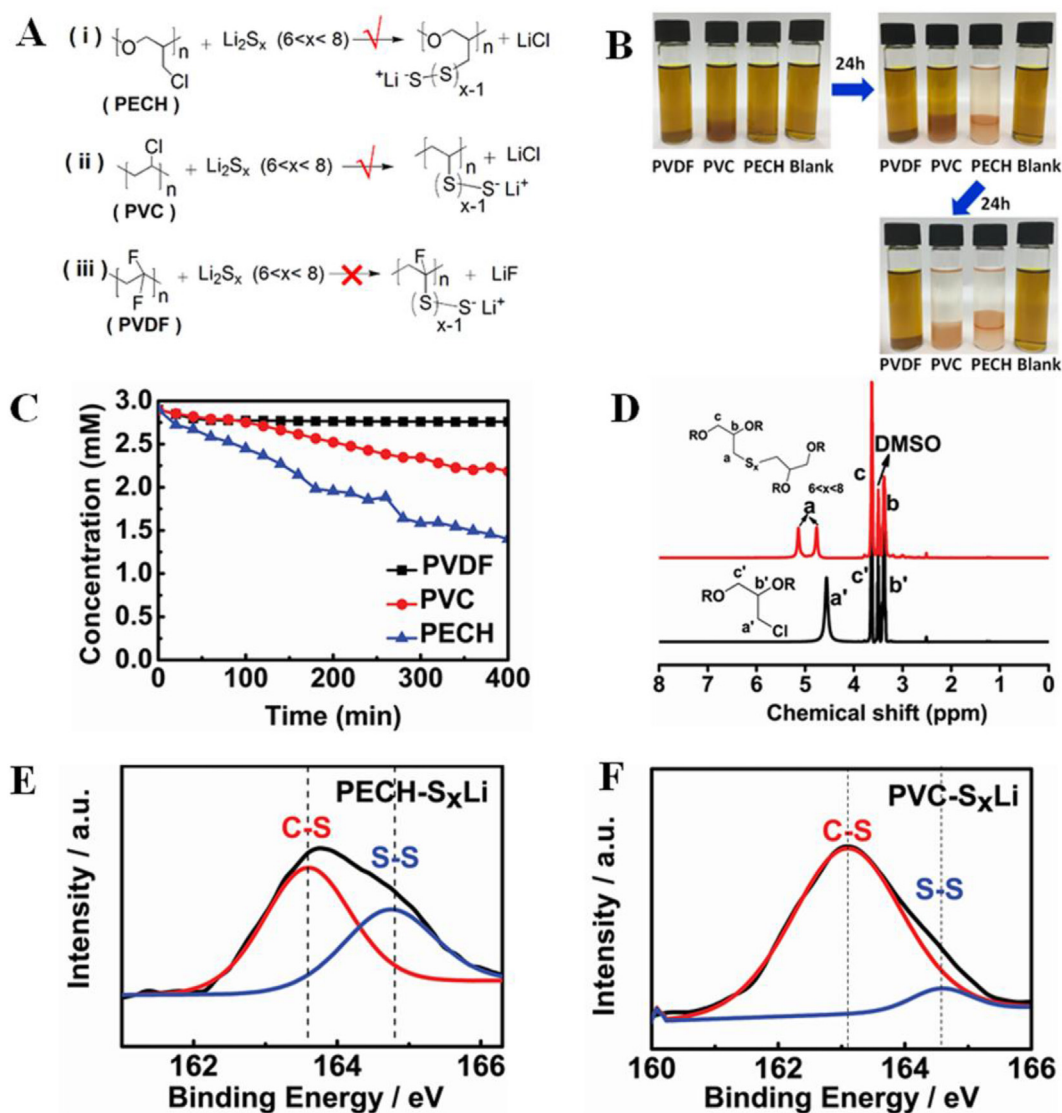


Fig. 1. A. Chemical capture of diffusing lithium polysulfides with active binders: PECH: polyepichlorohydrin and PVC: poly(vinyl chloride) in comparison to inactive PVDF: poly(vinylidene fluoride). B. Photographs of a polysulfide solution exposure to the different binders: PECH, PVC, PVDF and no binder (Blank). C. Time-dependent concentration for the different binders obtained from UV-vis absorption spectra recorded at room temperature. Characterization of chemical bond between binder and polysulfide: ^1H NMR spectroscopy D, XPS spectra for PECH-S_x E, and PVC-S_x F.

[17,18]. On the other hand, the polymeric binders have been shown to play vital roles in various Li-S batteries. Traditional binders are mainly chemical stable polymers such as poly(vinylidenedifluoride)(PVDF) [19,20], poly(vinylpyrrolidone)(PVP) [21], gelatin [22], styrene-butadiene rubbers (SBR) [23], etc. Binders with multi-functions, e.g., electronic conductivity, N-Li bonding, O-Li bonding electrostatic bonding ability, have recently been introduced into Li-S batteries with improved performances [24]. However, these polymeric binders haven't displayed exciting capability in limiting the shuttle effect of the polysulfides in the Li-S batteries.

Herein, we show that chemically active binders not only can bind the electrode to the current collector, but also immobilize the polysulfides from the electrolyte on to the electrode, thus achieving high-performance Li-S batteries. Specifically, two chemically active binders: polyepichlorohydrin (PECH) and poly(vinyl chloride) (PVC) are demonstrated in comparison with the traditional chemically stable binder PVDF. The chemical structures of these three binders are shown in Fig. 1A. PECH has a primary alkyl chloride and PVC has a secondary alkyl chloride in each repeat unit, while PVDF has two reactionless secondary alkyl fluoride. In the charge/discharge process, both PECH

and PVC are able to react with the formed polysulfide species Li_2S_x ($6 < x < 8$) to form binder-polysulfide compounds, due to the nucleophilic attack from sulfide ion of the polysulfide and the release of the LiCl to the electrolyte. Due to the strong electronegativity of the fluorine in PVDF, the replacement of fluoride by sulfide and the release of LiF to the electrolyte are not energetically favorable. Thus, with PECH and PVC, the formation of the binder-polysulfide compounds can successfully immobilize the polysulfide in the porous electrode, which is then connected electrically by acetylene black (AB) conductive additives [24–29].

2. Experimental

2.1. Cathode fabrication

All chemicals were purchased from Sigma-Aldrich and used without purification. The PVC and PVDF are first dissolved in NMP, while PECH is dissolved in chlorobenzene, all at 5 wt% ratio. Commercial micro-metric sulfur powder and acetylene carbon (C65) are added into the binder-solvent solution after the binder is dissolved. The weight ratio of

Download English Version:

<https://daneshyari.com/en/article/10154683>

Download Persian Version:

<https://daneshyari.com/article/10154683>

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