



On the dispersion of lithium–sulfur battery cathode materials effected by electrostatic and stereo–chemical factors of binders



Xiaoheng Hong^{a, b}, Jun Jin^a, Zhaoyin Wen^{a, b, *}, Sanpei Zhang^a, Qingsong Wang^a, Chen Shen^a, Kun Rui^a

^a CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China

^b ShanghaiTech University, Shanghai 200031, PR China

HIGHLIGHTS

- Binders disperse the cathode materials by electrostatic repulsion.
- Lower rotational barrier energy of the binder chains promises better dispersion.
- Higher charge densities of the binders enable better repulsion between the cathode materials.
- Charge-discharge performance is proved to be greatly effected by the cathode uniformity.

ARTICLE INFO

Article history:

Received 27 January 2016

Received in revised form

28 March 2016

Accepted 23 April 2016

Keywords:

Lithium–sulfur battery

Binder

Dispersion mechanism

Sulfur cathode

Cathode morphology

ABSTRACT

Sodium carboxymethyl cellulose–styrene butadiene rubber (CMC–SBR), sodium alginate (SA) and LA132 are utilized as the polymer binders for the cathodes of Li–S batteries to study their dispersion mechanism on the cathode materials and the consequent influence on the performance of Li–S batteries. Zeta potential tests, differential scanning calorimetry analysis and calculations of the rotational barriers of the links of the polymer chains by General Atomic and Molecular Electronic Structure System (GAMESS) reveal that higher charge densities and better chain flexibility of the binders promise the dispersion of the downsized cathode materials. LA132 is found to have optimal characteristic for dispersing and stabilizing the cathode materials in aqueous environment. The cycling performance and SEM images of the cathodes demonstrate that cathodes with higher dispersion degree achieve higher discharge capacities. The electrochemical impedance spectroscopy (EIS) results further support that better dispersed cathodes have lower impedance resulting from their well established conducting frameworks.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The continued demand for long-range electric vehicles is impelling the current electrical storage systems beyond the conventional lithium ion batteries. Based on the reversible electrochemical reaction: $S_8 + 16Li \leftrightarrow 8Li_2S$ [1], lithium–sulfur battery (Li–S) theoretically offers an energy density of 2600 Wh kg^{−1} and a specific capacity of 1675 mAh g^{−1}, demonstrating the potential for being a next-generation energy storage system. Nevertheless, Li–S suffers from capacity decay and self-discharge caused by both

polysulfide shuttle effect [2] and the insulating nature of the electrochemical reactive material S₈ and Li₂S/Li₂S₂ [3]. Before being scaled for industrial applications, Li–S is still faced with challenges.

To address this, one main strategy is to immobilize sulfur inside downsized conducting host materials e.g. mesoporous carbon [4,5], carbon nanotube [6,7], graphene [8,9], etc. These methods enormously enhance the performance of Li–S battery. However, when it comes to the industrialization of Li–S, the use of hydrophobic materials with high surface area that spontaneously over-aggregate [10,11] still complicates the fabrication of the cathode materials. Severe aggregation of cathode materials would take place when solvent is evaporated. This would lead to undesired pinholes or crackings, deteriorating the cycling performance [12] and causing unreliable quality from batch to batch [13].

To mitigate this, polymer binders play an important role. The

* Corresponding author. CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China.

E-mail address: zywen@mail.sic.ac.cn (Z. Wen).

basic function of a binder is to strongly interact with both the cathode material and the current collector to enable sufficient electrical contact and structural robustness. More significantly, to overcome the spontaneous over-aggregation, another required function of a binder is to modify the liquid-solid interface and disperse the downsized material homogeneously. Polyvinylidene fluoride (PVDF) serves as the most commonly used binder in lithium sulfur batteries for its strong adhesion strength and good electrochemical stability. However, the hydrophobic nature of it brings about the problem of swelling and dissolving in organic electrolyte. This would cause the gradual degradation of the conductive network. Moreover, the solvent for PVDF, *N*-methyl pyrrolidinone (NMP), is a hazardous organic solvent [14,15] with a boiling point of 230 °C. It requires high energy cost and processing complexity when being dried. In contrast, water base binders are better choices for Li-S application. They do not dissolve in electrolyte owing to the hydrophilic nature, and the solvent water is totally benign. The water based binders in common use are polyethylene oxide (PEO) [16], sodium carboxymethyl cellulose-styrene butadiene rubber (CMC-SBR) [17], sodium alginate (SA) [18], polyvinylpyrrolidone (PVP) [19], carbonyl- β -cyclodextrin [20], gelatin [21] and LA132 [22] (a copolymer of acrylonitrile, acrylamide and acrylic), etc. Among these, SA, CMC-SBR and LA132 are widely applied for dispersing and binding different types of sulfur cathode composites [23–27]. They are also of ionic nature originating from the carboxylate groups, which are able to disperse the hydrophobic particles through the electrostatic double-layer repulsion mechanism [28,29]. The electrostatic repulsing dispersability is practically helpful to impart stability and uniformity to the cathode slurry during coating and drying process, which is beneficial to the cycling performance of the cells fabricated.

In this study, we have investigated the electrostatic repulsing effects of these ionic binders on the cathode materials and their consequent impact on the electrochemical performance of the cells. The intensity of electrostatic double layer repulsion were examined by zeta potential tests. The different chain flexibilities of the binders that effects the electrostatic repulsion were studied by determining the glass transition temperature (T_g) using differential scanning calorimetry(DSC). The chain flexibilities were also explored by calculation of the rotational barriers of the polymer chains links using General Atomic and Molecular Electronic Structure System (GAMESS). Moreover, Li-S cells with SA, CMC-SBR and LA132 as the binder, respectively, were prepared and tested at controlled conditions in terms of sulfur loading, electrolyte volume, cutoff voltages and cycling rates etc. to manifest how dispersion morphology effects the cell performance. SEM images of the cathodes and the Nyquist plots of the cells are given to verify the discussion.

2. Experimental

2.1. Materials

The Sulfur-Ketjen Black composite (S-KB) was prepared via heating the mixture of KB and sulfur powder (weight ratio S: KB = 4:1) in a sealed container at 155 °C for 12 h. The conductive agent of Super P carbon black (SP) was used as received. The binders, LA132 (Indigo, Chendu, China), CMC (Mac 350HC, Nippon Paper, Japan), SBR (TRD 102A, JSR, Japan) and SA (Sino pharm Chemical Reagent Co., Ltd, China), were used as received.

2.2. Cathode preparation and performance test

The cathode slurry was composed of 80 wt% of S-KB, 10 wt% of Super P and 10 wt% of binders dispersed in water solvent. For CMC-

SBR binder, the weight ratio of CMC: SBR is 1:1. All the slurry was prepared by thoroughly mixing the components in deionized water using magnetic stirring for 10 h. The slurry was blade-coated onto Al foils. After that the cathode sheets were hot air dried and further vacuum-dried at 60 °C for overnight. The obtained cathode sheets were cut into 12 mm diameter discs with an average sulfur loads of around 0.7–1 mg cm⁻². 2025 coin-type cells were assembled in an argon-filled glove box (Super1220/750/900, MIKROUNA, Shanghai, China) with both H₂O and O₂ contents lower than 0.1 ppm. The electrolyte was composed of 1 mol L⁻¹ LiTFSI and 0.2 mol L⁻¹ LiNO₃ in a mixture of 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (1:1 vol ratio). Metallic lithium foils were used as the anodes and polymer membranes (SK, Korea) served as the separators. The volume of electrolyte for each cell was controlled at 40 μ L. The cells were tested at room temperature (approx. 25 °C) under galvanostatic condition at 0.2 C (335 mA g⁻¹). The cut off voltage was 1.8 V–2.8 V vs. Li/Li⁺. The charge-discharge test instrument was CT2001A from LAND Electronic Co., Ltd, China.

2.3. Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopies (EIS) of the cells were measured at the open circuit voltage on Autolab testing platform (Metrohm, Switzerland). The frequency range applied was from 10⁶ Hz to 0.1 Hz with an amplitude of 0.01 V.

2.4. Zeta potential test

S-KB were dispersed in aqueous solutions of CMC, SA and LA132 by ultrasonic treatment to give homogenous colloids. A series of colloids for each binder were prepared. The concentrations of S-KB were controlled at 4 μ g mL⁻¹ and the concentrations of the binder were 4, 8, 16 and 48 μ g mL⁻¹, respectively. The zeta potential of the particles were tested on Malvern Zetasizer Nano-ZS90.

2.5. Differential scanning calorimetry

DSC analysis was carried out on Mettler Toledo DSC 822. Before DSC analysis, the samples were vacuum dried at 60 °C for over night to dehumidify. 7.00 mg of LA132, 7.00 mg of CMC and 7.20 mg of SA were tested. The samples were heated from 25 °C to 180 °C at 5 °C min⁻¹.

2.6. SEM study

The morphology of the cathode of each binder, before and after the cycling tests, were observed using a scanning electron microscopy (SEM, S3400 N, Hitachi). Before the SEM observation, the cathode discs were gently rinsed in DME in the glove box to remove the LiTFSI remaining.

2.7. Peel test

180° peel tests were performed on a universal testing instrument (Instron-5592, Massachusetts, U.S.A.). The cathode film was sandwiched between a 3 M scotch tape and the Al foil. The peeling rate employed was 50 mm min⁻¹.

3. Results & discussion

Since the dried cathode retains the morphology of the wet state, the cathode morphology is dependent on the dispersion degree of the cathode slurry. In this way, the dispersability of the binder effects the electrochemical performance of a Li-S cell. The binders studied here, CMC-SBR, SA and LA132, are all of ionic nature

Download English Version:

<https://daneshyari.com/en/article/7727630>

Download Persian Version:

<https://daneshyari.com/article/7727630>

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