



Manganese modified zeolite silicalite-1 as polysulphide sorbent in lithium sulphur batteries



Vida Lapornik^a, Natasa Novak Tusar^{a, b}, Alenka Ristic^a, Rajesh Kumar Chellappan^c, Dominique Foix^{c, d}, Rémi Dedryvère^{c, d}, Miran Gaberscek^{a, b, d}, Robert Dominko^{a, d, *}

^a Laboratory for Materials Chemistry, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

^b Centre of Excellence for Low Carbon Technologies, Hajdrihova 19, 1000 Ljubljana, Slovenia

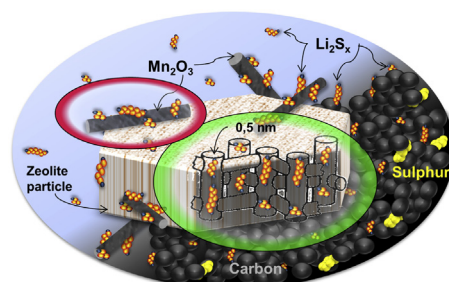
^c IPREM-ECP (UMR 5254 CNRS), University of Pau, Hélioparc, 2 av. Pierre Angot, 64053 Pau Cedex 9, France

^d Alistore – European Research Institute, 33 rue Saint-Leu, 80039 Amiens Cedex, France

HIGHLIGHTS

- Cycling can be improved by addition of zeolites in the cathode or as an interlayer.
- Zeolite MnS1 shows superior sorption properties in Li–S batteries.
- Sulphur content in the cathode depth was determined by FIB equipped with EDX.
- Interphases of cathode and anode were analyzed by XPS measurements.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 August 2014

Received in revised form

7 October 2014

Accepted 28 October 2014

Available online 30 October 2014

Keywords:

Lithium battery

Sulphur cathode

Sorption

Polysulphides

Cycling stability

ABSTRACT

Discharge/charge process of classical lithium sulphur battery proceeds through intermediate polysulphides which are soluble in classical electrolyte systems. Due to concentration gradient soluble polysulphides easily diffuse/migrate out from cathode composite forming non-uniform distribution of the sulphur within cathode. Eventually polysulphides can be completely reduced on the metallic lithium anode. In this work we compare the sorption properties of manganese modified zeolite silicalite-1 (MnS-1) with a cathode composite containing SBA-15 additive and a cathode composite without additive. Careful analysis using XPS and FIB microscopy equipped with EDX show improved retention of polysulphide species within cathode composite in the case of MnS-1 zeolite as an additive. Interestingly, the amount of sulphur species detected by XPS on the metallic lithium is very similar regardless on cathode composite we use. Finally, similar cycling behaviour can be observed if MnS-1 zeolite is used as an interlayer between composite cathode and separator.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Lithium–sulphur (Li–S) batteries are one of the most promising candidates to couple renewable energy sources for green transportation and large-scale energy storage – owing to their various desirable characteristics including competitive cost, and low environmental impact [1]. Moreover, their high theoretical energy density is estimated to be much higher than that of conventional Li

* Corresponding author. Laboratory for Materials Chemistry, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia.

E-mail address: robert.dominko@ki.si (R. Dominko).

ion batteries based on intercalation electrodes. Despite these advantages, massive implementation of Li–S batteries remains hindered by various challenges that partially arise from the cathode [2]. A major problem is the rapid capacity fading, predominantly due to dissolution of intermediate reaction (polysulphides – Li_2S_x). Once the polysulphide ions diffuse out from the nanostructured cathode, their reaction with the Li anode causes active mass loss. At the same time the redeposition of sulphide species from the electrolyte back onto the cathode surface generates a non uniform distribution of sulphur at the end of charge. The polysulphide anions also act as an internal redox shuttle, which gives rise to low coulombic efficiency [3].

In light of above, it is necessary to keep sulphur homogeneous deposition in the composite cathode. That can be achieved by several different approaches. For instance, many directions towards improved cathode architecture and chemical compositions have been proposed [4]. The most attractive and efficient seems to be the use of microporous carbon materials [5]. An improvement has been achieved by conductive carbon materials with uniform and controlled pore structures [6]. Due to conductive carbon framework, the sulphur stays within the carbon pores/channels thus maintaining the electrical contact. But improved electrical conductivity of the matrix does not solve the intrinsic problem of dissolution and migration of the polysulphides [3]. For that reason other approaches, like use of designed electrolyte systems (solvents, salts and salt concentration) [7], use of polymers [8] or/and modified separators [9] have been recently explored. Another possible way to suppress polysulphide migration is use of various oxide additives, such as V_2O_5 [10], Al_2O_3 [11], La_2O_3 [12], $\text{Mg}_{0.6}\text{Ni}_{0.4}\text{O}$ [13] and $\text{Mg}_{0.8}\text{Cu}_{0.2}\text{O}$ [14] particles that have been employed as adsorbents for polysulphides mixed with the sulphur/carbon composites. The small dosages of nano-sized additives simultaneously improved the discharge capacity, cycle durability of the electrode and increase of otherwise low coulombic efficiency.

The role of surface adsorption and pore absorption was studied with mesoporous silica (SBA-15) [15], mesoporous titania (TiO_2) [16] and metal-organic frameworks (MOF) [17]. The mesoporous silica SBA-15 is effective at retaining the soluble polysulphides due to its high surface area, large pore volume, bi-connected porous structure and highly hydrophilic surface properties. The surface Si–O groups serve as weak binding sites for polysulphides with the ability of releasing the active material for electrochemical reduction-oxidation [15]. Lee et al. [18] reported that size and shape of the pores as well as the pore size distribution and specific surface area have a major impact on the composite cathode's electrochemical performance. Smaller pore size leads to stronger interactions between the polysulphides and the pore walls due to the overlap of the adsorbate–adsorbent interactions potentials from both sides of the pore.

Herein, we propose the use of manganese doped zeolite silicalite-1 (MnS-1) [19] as an additive in the Li–S batteries. Silicalite-1 is microporous crystalline silica with a MFI topology consisting of two 10-ring channels intersecting with each other to form a three-dimensional porous framework [20]. Nano-sized zeolite crystals (around 200 nm) comprise interconnecting straight and sinusoidal channels with an elliptical pore opening and an average pore size of 0.5 nm. Incorporation of manganese into silicalite-1 framework via direct hydrothermal synthesis under microwave heating generates Mn^{3+} extra-framework where manganese is in the form of manganese oxide (Mn_2O_3) nano-particles [19]. Our MnS-1 zeolite material combines two types of additives in one, a highly ordered microporous silica structure within the individual zeolite particles together with nano-sized Mn_2O_3 particles. We demonstrate attractive performance of microporous

zeolite MnS-1 additive inside the cathode composite and we study its role as a deposit on the glass fibre separator. We compare the electrochemical performance of microporous zeolite MnS-1 additive with mesoporous silica SBA-15 [15] additive and with cathodes containing no additives. Improved electrochemical properties and cycling stability of cathodes containing silica is explained by effective adsorption/absorption of the polysulphides in the cathode which decreases their migration out from the cathode and the consequent irreversible reaction with lithium anode.

2. Materials and methods

2.1. Synthesis of zeolite MnS-1

Manganese silicalite-1 (MnS-1) nanosized crystals were synthesized under microwave-assisted hydrothermal syntheses [19]. The reaction mixtures were prepared from 34.72 g tetraethoxysilane (98%, TEOS) as silica source, 25.42 g tetrapropylammonium hydroxide (40%, TPAOH) as structure directing agent and 0.57 g manganese acetate (100%, $\text{Mn}(\text{CH}_3\text{COO})_2 \times 4\text{H}_2\text{O}$) as manganese source in 42.55 g of distilled water at room temperature. The prepared reaction mixtures were first aged for 1 day before hydrothermally treated in microwave. The removal of the structure directing agent was done by calcination at 500 °C in air flow. Si/Mn ratio was 100. The local environment of manganese in MnS-1 nanocrystals was characterized by Transmission Electron Microscopy (TEM) and X-ray absorption spectroscopy (XANES and EXAFS techniques – not shown in this work). The combined analysis of TEM images and XANES and EXAFS spectra revealed incorporated Mn^{3+} into the silicalite-1 framework as extra-framework manganese in Mn_2O_3 forms [19].

2.2. Synthesis of SBA-15

Ordered mesoporous silica SBA-15 powders were synthesized by dissolving 8 g of Pluronic[®] P123 triblock copolymer in the mixture of 260 mL of distilled water and 40 mL of concentrated hydrochloric acid (37 wt. %, HCl) [21]. Then 17 mL of TEOS was added under stirring at 45 °C. The reaction gel was stirred for 8 h at 45 °C and aged for another 16 h at 80 °C. The obtained gel with molar ratios of reaction components SiO_2 : P123: HCl: H_2O = 1: 0.017: 5.85: 190 was hydrothermally treated in Teflon-lined autoclave at 100 °C for 24 h. The obtained product was continuously washed with distilled water and dried at room temperature. The surfactant was removed by calcination at 550 °C for 6 h in an air flow.

2.3. Preparation of silica/carbon/sulphur composites

First, the zeolite MnS-1 was dried in vacuum for 24 h at 80 °C. A mixture of zeolite MnS-1 (11.25 wt. %), Printex XE2 (Degussa) carbon black (26.25 wt. %) and sulphur (62.5 wt. %) were ball milled at 300 rpm for 30 min and heated to 155 °C for 5 h with a 0.2 °C Cmin^{-1} heating ramp under argon flow. The same procedure was also applied with (11.25 wt. %) SBA-15 additive. According to elemental analysis, the composites after impregnation at 155 °C contains 62.5 wt. % of sulphur.

2.4. Preparation of silica/glass fibre separator

Zeolite MnS-1 (0.5 mg) was dispersed in water (0.5 mL) by an ultrasound for 30 min. Glass fibre separator was cut on discs (4.15 cm^2) and covered with zeolite suspension. The soaked separators were dried in vacuum at 90 °C for two days.

Download English Version:

<https://daneshyari.com/en/article/7735258>

Download Persian Version:

<https://daneshyari.com/article/7735258>

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