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Short communication

Activation of micropore-confined sulfur within hierarchical porous carbon for lithium-sulfur batteries

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HIGHLIGHTS

- Activation process of voltage plateau at 1.75 V during discharge is revealed.
- The reversible reaction appears upon cycling at 0.1C between 1 and 3 V.
- Micropore confined sulfur's role in the activation is elucidated.

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ABSTRACT

Hierarchical porous carbon is often used in Li–S batteries due to the widely perceived benefits regarding the wide range of pore sizes. However, such notions are based solely on demonstrations of improved cyclic performances, and specific evidence to prove the utilization of the pores is yet to be found. Herein, we report, for the first time, the evidence for gradual activation of micropore-confined sulfur within porous carbon structures. By systematic comparison of microporous and hierarchical porous structures, we show that at sufficiently low current, sulfur infused hierarchical porous structures display a slowly activated and reversible reaction at 1.75 V vs Li/Li⁺ during discharge. This is in addition to the conventionally reported two voltage plateau at 2.3 and 2.1 V. Furthermore, the effects of LiNO₃ decomposition on the system and the electrochemical mechanism behind the activation process is elucidated. Overall, the findings supplement the currently known electrochemical mechanisms occurring within porous structures and pave the way for more efficient utilization of hierarchical porous structures for applications in Li–S batteries.

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1. Introduction

Hierarchical porous structures, consisting of micro- and mesopores, are often thought to improve both specific capacity and rate capability of energy storage materials [1–15]. In Li ion batteries, papers have reported that mesopores enhance electrolyte diffusion within the pores, whereas micropores significantly increase the

surface area and active sites [4,7–9,11–13]. Similar material design concepts have been applied to Li–S batteries. In addition to the aforementioned benefits occurring in Li ion batteries, micropores are “designed for encapsulating/immobilizing the active material” [2] to alleviate polysulfide dissolution [16–23], a major problem in Li–S batteries. Such features have been repeatedly mentioned to highlight hierarchical porous carbon structure as an excellent material design.

Despite rapid improvements in performance, the complex electrochemical mechanism within the porous structures is yet to be fully understood. Several research groups have identified that characteristic two voltage plateau at 2.3 and 2.1 V (vs. Li/Li⁺) arise from conversion of solid S₈ to soluble polysulfide and then from polysulfide to solid Li₂S, accordingly [2,24–26]. However, a

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question still remains as to whether and how the sulfur confined in micro- and mesopores are utilized.

On a related note, several groups have reported sulfur infused into microporous structures display only a single plateau starting around 1.6–1.8 V [27–29]. Wan et al. reason that small sulfur molecules, S_{2-4} , are confined in small micropores and are free of polysulfide dissolution, hence the omission of first plateau (~2.3 V) [27]. Huang et al. further elaborate that solid–solid reactions occur with small micropore-confined sulfur that causes high resistance, resulting in a Li_2S formation reaction occurring below 1.8 V with overpotential [28]. It's more likely that the micropore-confined sulfur has a thermodynamically lower reduction potential. For such reasons, the cells are discharged to 1.0 V, applying low current (0.1C) to fully lithiate the micropore-confined sulfur [27,28]. In contrast, hierarchical porous structures are often discharged to 1.5 V and/or apply 1C [16–21], which are higher and faster than those reported to lithiate micropore-confined sulfur [27–29].

In order to investigate whether the sulfur infused inside micropores within hierarchical porous structures can be utilized as intended, the electrochemical reaction of sulfur infused 1) small micropore carbon (SMC) and 2) hierarchical microporous carbon (HMC) are compared. The results are further corroborated with voltage profiles of sulfur infused 3) mesoporous carbon (MC). The findings reported in this paper suggest, for a hierarchical porous structure, there exists a kinetic barrier that must be overcome to utilize its micropore-confined sulfur.

2. Experimental

2.1. Synthesis of SMC

SMC was synthesized according to a previous work [30]. Resorcinol and formaldehyde were mixed with a solution containing deionized water and aqueous ammonia (28% NH_3). After stirring for 24 h at room temperature, the solution was moved to an oven and heated for 24 h at 90 °C without stirring. The solid product was recovered by centrifugation and was washed several times with deionized water. For the carbonization, the products was then heated to 800 °C under a N_2 atmosphere over 3 h at a heating rate of 4.3 °C min^{-1} .

2.2. CO_2 activation of SMC to obtain HMC

SMC in an alumina boat was placed in a quartz tube purged with flowing nitrogen. The sample was then heated to 900 °C and then the gas flux was changed to carbon dioxide for 2 h.

2.3. Synthesis of MC

MC was prepared using a nanocasting method as shown in our previous report [31]. A mesoporous silica template (Fig. S1 and S2) was first synthesized using the modified stöber method based on the surfactant (CTAB) micellization with a silica source. Phenolic resin was used as the carbon source and it was incorporated into the mesoporous silica nanoparticle via acid site specific gas phase polymerization of phenol and paraformaldehyde. Then, the carbon source incorporated samples were carbonized at 800 °C for 3 h. In order to remove the silica template, the carbonized product was immersed in 6 M aqueous KOH solution at 180 °C overnight. The etched product was fully washed by DI water and recalcined at 800 °C for 1 h before use.

2.4. Preparation of carbon-sulfur composites and mixtures

Sulfur (Alfa Aesar) and a corresponding porous carbon (SMC,

HMC, MC) were mixed in the following mass ratio; $m_s:m_c = 50:50$ for SMC_17S, 67:33 for HMC_40S, 70:30 for HMC_50S, 72:28 for HMC_65S, and 50:50 for MC_40S. Each mixture was sealed in a SUS container (Fig. S3) and heated at 155 °C for 6 h and then heated at 300 °C for 1 h for SMC_17S and 2 h for the rest to remove excess sulfur. SMC and S Mixture and HMC and S Mixture were prepared with the same sulfur to carbon weight ratio as that of SMC_17S and HMC_40S, accordingly.

2.5. Characterization

X-ray powder diffraction (XRD) was collected using Rigaku (D/MAX 2500). The Raman spectra were recorded with a Horiba Jobin-Yvon LabRam Aramis spectrometer. X-ray photoelectron spectroscopy (XPS) was performed using Sigma Probe (ThermoFisher Scientific). The cycled electrodes were extracted within a glove box and then washed with solvent (DOL:DME) three times for the XPS analysis. Nitrogen sorption experiment was carried out using BELSORP-max. Scanning electron microscopy (SEM) images were observed with FE-SEM (SIGMA, CARL Zeiss) and transmission electron microscopy (TEM) images and EDS were obtained using JEOL EM-2010 microscope. Thermogravimetric analysis (TGA) analysis was done in a Nitrogen atmosphere with a temperature ramp of 10 °C (TA Instruments TA SDT Q600).

2.6. Electrochemical measurements

The active material, super P, and polyvinylidene fluoride (70:10:20) were mixed using n-methyl-2-pyrrolidinone as the solvent. The slurry was pasted on an Al foil via doctor blade method. An active material loading of ~0.5 $mg\ cm^{-2}$ was used. Lithium foil was used as the anode and the separator was obtained from SK chemical. 1 M LiTFSI in a mixture of DOL and DME (1:1 by volume) with 0.1 M $LiNO_3$ was used as the electrolyte (Panax Starlyte). The galvanostatic cycling was performed using 2032 coin cells and carried out on a WBCS3000 (Wonatech System, Korea). For the galvanostatic intermittent titration technique (GITT), a current pulse of 167.5 $mA\ g^{-1}$ was applied for 5 min to measure the closed-circuit voltage (CCV) and then turned off for 10 min to measure the quasi-open-circuit voltage (QOCV) (Fig. S4). The current density and specific capacity were calculated based on the weight of sulfur. Electrochemical impedance spectroscopy was tested after a period of rest on Zennium (Zahner) in the frequency range from 100 KHz to 10 mHz with an amplitude of 5 mV.

3. Results and discussion

As a model system, SMC that is synthesized via carbonization of monodisperse polymer spheres (Fig. S5) [30], and HMC whose pore size and surface area are increased via CO_2 activation process using SMC are employed. The SEM and TEM images of SMC and HMC in Fig. 1a and c show smooth surfaces and monodisperse particle sizes [31,32]. XRD analysis shows more featureless pattern of HMC around 24° than that of SMC (Fig. 1e). The increased disorderedness of HMC is confirmed under Raman spectra (Fig. S6), in which the ratio of I_D/I_G bands increases from 0.962 to 1.042 after CO_2 activation of SMC [33].

N_2 sorption data shows a typical type I isotherm for SMC (Fig. 1f inset), corresponding to microporous features (0.234 $cm^3\ g^{-1}$). In comparison, increased uptake at low pressure for HMC indicates that the microporosity has increased (1.227 $cm^3\ g^{-1}$). Calculated from the density functional theory (DFT) method, SMC contains pores smaller than 1.2 nm, whereas HMC has micropores and mesopores of size up to 4 nm (Fig. 1f). Table S1 summarizes the textural properties.

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