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Improved electrochemical performance of a three-dimensionally ordered mesoporous carbon based lithium ion battery using vinylene carbonate

Jung-Joon Kim[a,b], Chiyeong Ahn[a,b], Woojeong Bak[c], Won Cheol Yoo[c,*], Yung-Eun Sung[a,b,**]

[a] Center for Nanoparticle Research, Institute for Basic Science, Republic of Korea
[b] School of Chemical and Biological Engineering, Seoul National University, Seoul 151-742, Republic of Korea
[c] Department of Applied Chemistry, Hanyang University, Ansan, Gyeonggi-do 426-791, Republic of Korea

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ABSTRACT

The effects of vinylene carbonate (VC) as an electrolyte additive on a 3-dimensionally ordered mesoporous carbon based lithium ion battery are investigated. Our investigation reveals an optimal concentration of VC, which improves the discharge specific capacity at the 100th cycle to 844.3 from 684.3 mAh g^{-1}, and improves the first cycle's coulombic efficiency to 32.4 from 23.7%. The improvements are revealed to be a result of reduced charge transfer and solid electrolyte interface resistance, enabling better permeability of Li ions. This work demonstrates that VC is a viable electrolyte additive in improving the performance of a non-graphitic carbonaceous material.

1. Introduction

Vinylene carbonate (VC) is a commonly used electrolyte additive, which is reported to improve the properties of the solid electrolyte interface (SEI) formed on the surface of the electrodes [1,2]. When VC is used in a lithium ion battery, it is reduced prior to other electrolyte solvents and creates an improved SEI layer. The resulting positive effect includes the reduction of an irreversible capacity [2–5], the suppression of co-intercalation of solvents [6,7], and the improvement of cycling performance at elevated temperatures [3,4,7,8]. While the improvement has been reported in both cathodes and anodes [9–11], generally the enhancement has been mainly attributed to the graphite negative electrode [6,7,10–13]. The effect of the VC derived SEI on other carbonaceous materials, such as a porous carbon with high surface area [14,15], has not been investigated for lithium ion batteries. Due to the large number of defects, porous carbon with high surface area produces a thick SEI layer, which impedes Li ions diffusion [16,17]. Therefore, an enhancement of the properties of SEI could improve the performance of the porous carbon based lithium ion battery.

Herein, we report on the improved coulombic efficiency and the enhanced discharge capacity of a 3-dimensionally ordered mesoporous carbon (3DOmC) based lithium ion battery at room temperature using VC. A VC concentration that induces the formation of an optimal SEI is identified, and the underlying mechanisms of the improvement in performance are investigated.

2. Experimental

2.1. Synthesis of silica nanoparticles

Monodisperse silica nanoparticles were produced by the modified Stöber method that utilized L-lysine as a catalyst as shown in our previous work [18].

2.2. Synthesis of three-dimensionally ordered mesoporous carbon

3DOmC was synthesized by the infiltration of furfuryl alcohol to the close-packed silica nanoparticle arrays as shown in a previous work [19].

* Corresponding author. Fax: +82 31 400 5457.
** Corresponding author. Fax: +82 2 888 1604.
E-mail addresses: coolahella@snu.ac.kr (J.-J. Kim), acy6480@snu.ac.kr (C. Ahn), vince87@naver.com (W. Bak), wcyoo@hanyang.ac.kr (W.C. Yoo), ysung@snu.ac.kr (Y.-E. Sung).

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2.3. Electrochemical measurements

3DOmC, super P, and polyvinylidene fluoride in a weight ratio of 8:1:1 were mixed with *n*-methyl-2-pyrrolidinone as the solvent. The slurry was pasted on an Al foil via the doctor blade method. Lithium foil was used as the anode, and a separator from SK chemical is used. The standard electrolyte (SE) used for the electrochemical test was 1 M $LiPF_6$ in a mixture of EC and DMC (1/1, v/v) (Panax Starlyte). 3, 5, 10, and 20 wt.% of VC (Aldrich) were added to the SE, and they are referred to as 3VC, 5VC, 10VC, and 20VC, respectively. The galvanostatic cycling was performed using the 2032 coin cells and carried out on a WBCS3000 (Wonatech System, Korea) at a rate of 100 mA/g with a cutoff voltage of 3.0–0.001 V vs Li/Li^+ at room temperature. EIS was tested on Zennium (Zahner) in the frequency range from 100 KHz to 10 mHz with an amplitude of 5 mV.

2.4. Characterization

The SEM images were observed with a SIGMA (CARL Zeiss) and the TEM images were obtained using a Tecnai F20 (FEI). The small-angle X-ray scattering (SAXS) measurement was taken on a SmartLab (Rigaku) using Cu Kα radiation (45 kV, 200 mA). X-ray powder diffraction (XRD) was collected using a D/MAX 2500 (Rigaku) with Cu Kα (40 kV, 200 mA). The Raman spectra were recorded with a Horiba Jobin-Yvon LabRam Aramis. Nitrogen sorption experiment was carried out using BELSORP-max. Barrett–Joyner–Halenda (BJH) and the density functional theory (DFT) method are used to calculate the mesopores' and micropores' size distribution, respectively. XPS analysis was performed using a Sigma Probe (ThermoFisher Scientific) with Al Kα (1486.6 eV) as the X-ray source. The cycled electrodes are extracted within a glove box, washed with the solvent (DMC), then dried overnight before XPS and TEM analyses.

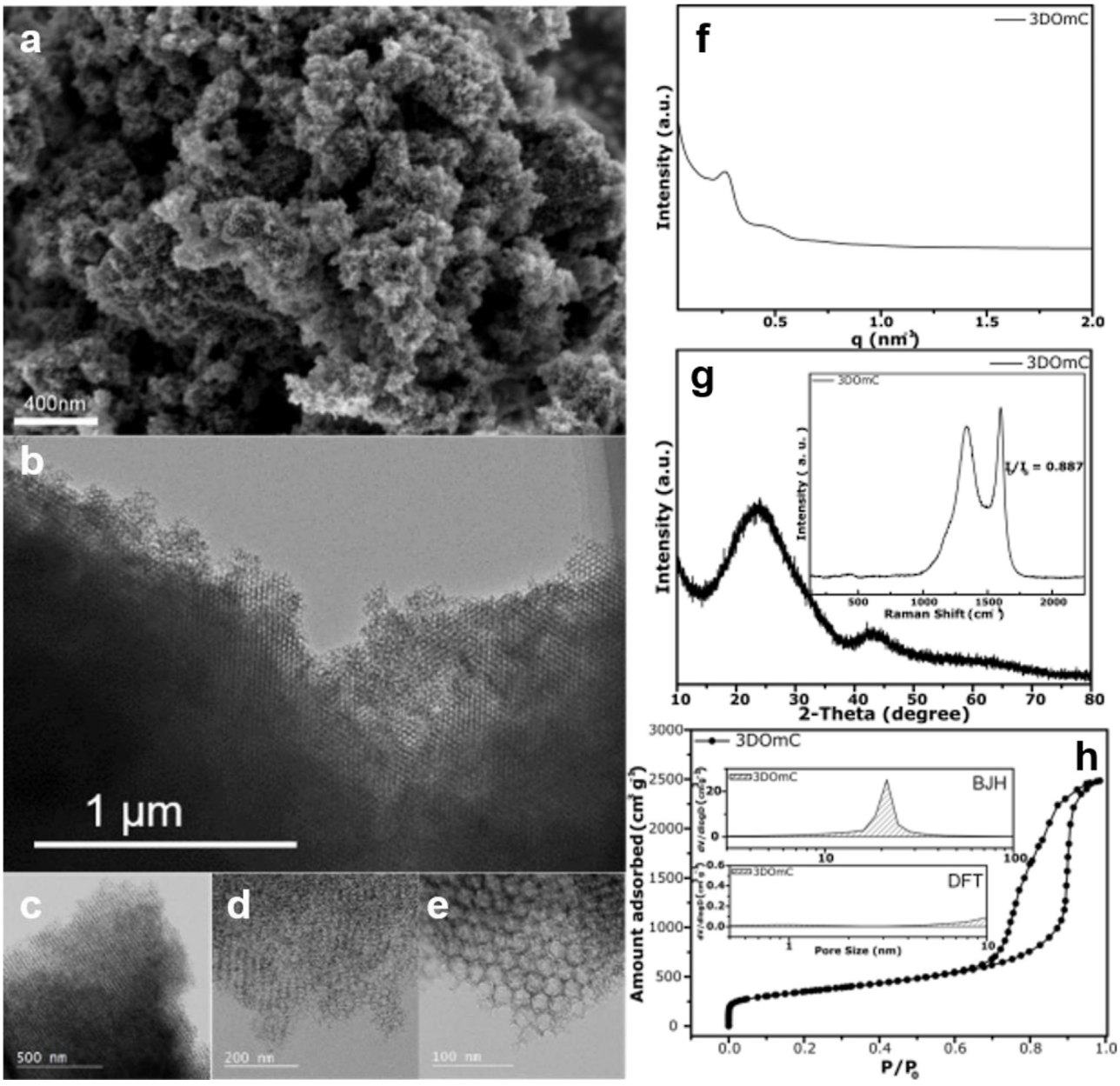

Fig. 1. (a) SEM and (b–e) TEM images of 3DOmC. (f) SAXS pattern, (g) wide-angle XRD pattern (inset: Raman spectrum), and (h) N2 sorption isotherm of 3DOmC (inset: pore size distribution using the BJH and DFT method).