Nanoporous hard carbon microspheres as anode active material of lithium ion battery

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ABSTRACT

Nanoporous hard carbon microspheres (NHCSs) were prepared by combination of microemulsion and polymerization methods and using phenolic resin (resol) as precursor and ethanol and ethylene glycol (EG) as solvent and soft template, respectively, followed by carbonization process. Using different amounts of EG resulted in NHCSs with different crystalline structure, surface area and pore volumes, and Li ion storage capacity, as evidenced by physical and electrochemical measurements. Higher and lower polymerization rates were also tested on the starting resol solution with composition which led to the NHCS with the highest surface area and Li ion storage capacity. The sample polymerized at higher rate had the highest surface area and pore volume, as well as the best Li ion storage performance in terms of capacity and rate capability. for all of the NHCSs, the specific surface area and Li ion storage capacity were well correlated, and a good correlation was observed between total pore volume and rate capability. Furthermore, acceptable correlations were found between Li ion storage capacity and either surface area or microstructure of the NHCSs.

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1. Introduction

Since their commercialization by Sony Energy Devices Corp. (formerly Sony Energy Tec Corp. between 1986–2000) in early 1990s [1], Li ion batteries (LIBs) have gained popular interest, due to such advantages, over their rechargeable battery counterparts, as high energy density [2], no memory effect [3], and slow self-discharge [4–6]. These advantages made LIBs a suitable electric energy storage tool for powering portable devices and electric vehicles [7,8]. However, like many other widely used technologies, there are continuous efforts for upgrading performance characteristics of these batteries, either to better fit current applications or even to become suitable toward new applications. Nowadays, carbonaceous materials are the mostly used anode active materials in LIBs, among which graphitic anodes are more common owing to their low working potential, high reversible capacity, and good cycling behavior [9,10]. However, as alternative, other carbonaceous materials such as hard carbons (HCs) have been investigated to enhance performance characteristics of LIB anodes [11–13]. HCs are a type of carbons with disordered structures and no long-range order (turbostratic carbon) that cannot be graphitized upon high temperature treatment [14,15]. Owing to their special structure, HCs have better performance characteristics in terms of capacity, rate capability, cycle life, and safety but they show low initial coulombic efficiency and high voltage hysteresis [16–25]. This type of carbonaceous materials is produced from such natural or synthetic polymeric precursors as sucrose [26], starch [27], phenolic resin [19], and pitch [28].

In order to improve electrochemical performance of HCs toward Li storage, some strategies such as synthesis of porous and/or spherical structures have been adopted [12,16,24,26,27,29–37]. Porous structure can act both as buffer against the volume change during the Li intercalation and as an electrolyte reservoir. These lead to longer cycle life (due to structural stability) and higher rate capability of porous HCs. Moreover, the advantages of having spherical structure are similar to those of mesocarbon microbead (MCMB), e.g. easier packing in the electrode.

Here, we report microemulsion-mediated hydrothermal synthesis of nanoporous hard carbon microspheres (NHCS) from resol-type phenolic resin in the presence of different amounts of ethylene glycol (EG) as pore-former. Elevated temperature helps cross-linking of the resol micro droplets, and at the same time, EG acts as a soft template. The influence of EG content and polymerization rate on the structure and Li ion storage performance of the NHCSs will be presented and discussed.

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2. Experimental Section

2.1. Synthesis of nanoporous microspheres hard carbon

The synthesis procedure was mostly adopted from British American Tobacco PLC patent [38]. Industrial grade resol resin (Resitan Co., Iran, 300–500 polymeric units) was mixed with ethylene glycol and ethanol (Table 1) at elevated temperature and with stirring to obtain a clear viscous solution. Addition of different amounts of ethanol was indispensable to obtain stable micro-emulsions. The as-obtained solution was then poured into stirring oil solution which itself comprised mineral oil containing 0.5% of the drying oil (varnish dispersed in hexane with cobalt (II) ethylhexanoate as curing agent, in a volume ratio of 1:4:1). The stirring mixture (microemulsion) was heated from ambient temperature to 160 °C at a rate of 5 °C per minute, soaked at this temperature for 20 minutes to ensure complete cross-linking, and subsequently cooled to room temperature. Afterwards, the obtained cured resin microbeads were filtered off from the oil, and as far as possible were washed with acetone and hot water to remove the residual oil and pore-former (EG). Then, the beads were dried under vacuum for 15 h and carbonized by heating at a rate of 5 °C per minute up to 700 °C and soaking for 4 h in tube furnace under argon atmosphere. After carbonization, the obtained samples were washed with concentrated hydrochloric acid and hot water followed by drying under vacuum for 15 h. It should be noted that if the resin beads are carbonized directly after separation from the oil, without washing, the porosity of resulting carbons decreases [39].

To examine the effect of polymerization rate, the composition of NHCS-2 (Table 1) precursor solution was chosen and polymerized with two further different rates; a faster and a slower, whose derived carbons are hereinafter denoted as NHCS-6 and NHCS-7, respectively. For the synthesis of NHCS-6, the precursor solution was poured into preheated (160° C) stirring oil solution. The temperature of the resulting mixture dropped to about 120° C, and cross-linking occurred normally within 1 to 2 minutes. The resulting suspension was then heated to 160° to complete the curing process. The remaining processes were as above for other NHCSs. NHCS-7 was synthesized just like NHCS-2, except that the mixture was heated to 160° at a rate of 3 °C per minute.

2.2. Physical Characterization

X-ray diffraction (XRD) experiments of the NHCSs were carried out over angular range from 5° to 80° with a step size of 0.05° using a PW1720 X-ray Diffractometer (Philips instrument) equipped with Cu Kα radiation (λ = 0.15406 nm). The average crystallite sizes have been estimated using the Scherrer equation

$$d = k \, \lambda / \beta \, \cos\theta \tag{1}$$

where k is the shape factor whose value is 0.9 and 1.84 for micro crystallite height (L_c, the crystallite size in c-axis direction) and

micro crystallite width (L_a, the crystallite size in a-axis direction), respectively, λ is the X-ray wavelength (0.15406 nm for Cu Kα), β is the full-width at half-maximum for peak at 2θ, and θ is the angle of the diffraction peak. L_c and L_a values were calculated from the β of (002) and (100) peaks, respectively. R parameter was calculated from (002) peak [23]. Raman spectra were recorded on Bruker Senterra Raman microscope using an excitation laser of 532 nm. Peak intensities and surface areas were extracted from Raman spectra by PeakFit version 4.12 software. FT-IR spectra were recorded on a JASCO 6300 spectrometer over the wavenumber range of 400–4000 cm^{-1}. Optical images of the NHCSs were recorded using a Nikon YS100 optical microscope equipped with 2 mega pixel digital camera, and diameters were measured by Microstructural Image Processing software (MIP 4.1 full, Nahamin Pardazan Asia, I.R. Iran). Scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDAX) were conducted on a VEGA3 XMU instrument (TESCAN).

Nitrogen adsorption–desorption measurements (Japan, BEL-SORP-Mini II) were carried out at liquid nitrogen temperature (77 K). Before sorption measurement, the samples were degassed for 48 h under vacuum at 250 °C. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method applied to the adsorption branch of the isotherms, and pore size distributions were derived using the Barrett–Joyner–Halenda (BJH) analysis.

2.3. Electrochemical measurements

The charge-discharge experiments were carried out on 128 battery tester (Kimia Pardaz Samaneh Co, I.R.Iran) with dedicated software (Kimiastat Analyzer software, Version 7.0.5). A homemade two electrode electrochemical cell (similar to Swagelok-type cells) was used throughout. Pure Li foil was used both as counter and reference electrode, and a porous polyolefin membrane was used as the separator. A typical working electrode was fabricated as follows: NHCS (92 wt %) was mixed with polyvinylidene fluoride (PVDF, 5 wt %) in 1-Methyl-2-pyrrolidone (NMP) and carbon black (3 wt %). The obtained slurry was simultaneously stirred and degassed under vacuum for 40 minutes, and coated (140 μm) onto a 10 μm thick copper foil current collector using a micrometer adjustable film applicator. The as-prepared electrode was dried at 120 °C for about ten minutes, roll-pressed several times to enhance inter-particle contact, adjust the film thickness, and help to better adhesion to the current collector. A typical final thickness of the electrode after being dried and roll-pressed was 30 μm. The electrode was then punched in the form of disks with a diameter of 10 mm, and dried at 120 °C for 15 h under vacuum. A typical loading mass was 0.3 mg cm^{-2}. A dried 1 M solution of LiPF$_6$ dissolved in a 1:1 (V/V) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte. All cells were assembled in a carefully dried glove box filled with high purity argon at room temperature.

To assess full capacity and cyclability, charge–discharge cycles of the NHCSs electrodes were carried out as follows: charging at

Table 1
Composition of the resole solutions containing pore former and codes of the corresponding carbons, as well as average size of NHCSs; Numbers in parentheses are 95% confidence limits of the average diameters.

Carbon code	Polymerization rate	Resole (g)	Ethylene Glycol (ml)	Ethanol (ml)	Average Diameter (μm)
NHCS-1	Medium	5	0	16	22 (5.6)
NHCS-2	Medium	5	5	16	19 (2.6)
NHCS-3	Medium	5	10	25	15 (2.9)
NHCS-4	Medium	5	15	40	5 (0.6)
NHCS-5	Medium	5	20	50	6 (0.5)
NHCS-6	High	5	5	16	33 (8.9)
NHCS-7	Low	5	5	16	5 (0.3)