Journal of Physics and Chemistry of Solids 86 (2015) 215–222

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Cellulose-based carbon—A potential anode material for lithium-ion battery

Krzysztof Kierzek*, Aleksandra Piotrowska, Jacek Machnikowski

Division of Polymer and Carbonaceous Materials, Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-344 Wrocław, Poland

ARTICLE INFO

Article history:
Received 5 May 2015
Received in revised form
19 June 2015
Accepted 21 July 2015
Available online 22 July 2015

Keywords:
Microporous materials
Vapor deposition
X-ray diffraction
Electrochemical properties
Microstructure

ABSTRACT

A series of hard carbons was produced by the carbonization of microcrystalline cellulose powder in the temperature range of 950–1100 °C. The properties of the carbons were characterized using elemental analysis, X-ray diffraction and N_2 and CO_2 adsorption. The effect of heat-treatment temperature (HTT), pyrolytic carbon (PC) coating and discharging mode on the lithium insertion/deinsertion behavior of the carbons was assessed in a coin-type half-cell with metal lithium cathode. Increasing cellulose HTT modifies mostly carbon porosity, the surface area (S_{DFT}) decreases from about 500 to 167 $m^2 g^{-1}$. It is associated with lowering the reversible C_{rev} and irreversible C_{irr} capacities, but without improving relatively low (0.72) 1st cycle coulombic efficiency. Applying constant current (CC)+constant voltage (CV) discharging mode instead of conventional CC enhances the reversible capacity by 15–18%. PC coating is effective in reducing C_{irr} by ~20% with a little change of C_{rev}. The best capacity parameters, C_{rev} of 458 mA h g^{-1} and C_{irr} of 139 mA h g^{-1}, were measured for PC coated 1000 °C carbon. The prolonged cycling of full-cell assembled with anode of the carbon and commercial cathode revealed that after initial 20 cycles the capacity decay (0.029 mA h/cycle) is comparable to that of commercial cell with graphite-based anode.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

High storage capacity, high current discharge and excellent cycle durability cause that lithium-ion batteries (LiB) have at present well established leading position amongst power sources for portable electronic devices [1]. A very attractive new field of application of the batteries are electric-powered vehicles. Recent forecast shows that in 2018 year the automotive application can constitute about half of demand for lithium-ion batteries which is estimated to about 95 GW h [2]. The development of better performing inexpensive anode material to replace graphite is one of challenges in further expansion.

Non-graphitizable "hard" carbons have received in the past a considerable attention as an anode material of lithium-ion battery [3–11]. This vast category of carbons comprises materials which are produced by heat-treatment of various natural and synthetic organic precursors of polymeric or macromolecular nature. The characteristic features of anode made of hard carbon heat-treated at about 1000 °C is enhanced, compared to graphite, capacity for electrochemical lithium storing together with some drawbacks: excessive irreversible trapping of lithium during the first discharging cycle, large hysteresis in the voltage profile and a considerable part of insertion occurring at the potential near 0 V versus Li/Li^+.

The electrochemical behavior is commonly attributed to the degree of structural ordering occurring in the carbons. In general, they are composed of distorted graphene layers, occurring singly or stacked to form basic structural units (BSU), which are randomly oriented and cross-linked [12,13]. Different extent of microporosity development is usually associated with such an arrangement of the matter. The heterogeneous disordered structure implies diverse mode of lithium bonding with the host lattice [14–16]. In addition to intercalation in between graphene layers, there occur interactions with active sites associated with the edges, structural defects and heteroatoms as well as filling microcavities with pseudo-metallic lithium clusters. Weak interaction between lithium atoms and poorly organized matter around pores is responsible for voltage hysteresis and the gradual destruction of the matter for capacity fading during cycling [17].

Structural and textural versatility of different origin hard carbons induces different behaviors during electrochemical charging and discharging. The comparative study of carbons prepared at 1000 °C from several common polymers pointed-out to cellulose as one of the most promising precursors of anode material [10].

* Corresponding author. Fax: +4871 3206203.
E-mail address: krzysztof.kierzek@pwr.edu.pl (K. Kierzek).

http://dx.doi.org/10.1016/j.jpcs.2015.07.015
0022-3697/© 2015 Elsevier Ltd. All rights reserved.

The cellulose-based carbon showed high first cycle lithium uptake, corresponding to 535 mA h g^{-1}, and the reversible capacity exceeding that of graphite. The inexpensive precursor and a facile synthesis route are in favor for using cellulose-based carbon as anode material for medium and large scale batteries of common use.

Cellulose derivatives, like methylcellulose and hydroxyethyl cellulose, are intensively studied for gel polymer electrolyte membrane [18,19]. However, cellulose itself has received so far rather little attention as a possible precursor of anode material of lithium ion battery. Interestingly, earlier studies [20,21] suggest that the lithium insertion/deinsertion behavior of cellulose-based carbons depends to a large extent on the preparation procedure applied. Therefore, the present work is an attempt to elucidate the effect of heat-treatment temperature and coating with pyrolytic carbon on the structural/textural properties and electrochemical performance of cellulose-based carbons. Moreover, constant current+constant voltage (CC+CV) discharge mode has been applied, in addition to simple one step CC mode, to assess the influence on the capacity and cycle durability. While basically the study was performed in a typical research half-cell with lithium metal as a counter electrode, the selected material was also tested in a full cell with a commercial lithium transition metal oxide cathode.

2. Experimental

2.1. Preparation of cellulose-based carbons

Microcrystalline cellulose (CEL) powder from Aldrich was used as a starting material. Pyrolysis/carbonization of cellulose was performed in a horizontal tube furnace by heating under nitrogen to 950, 1000, 1050 and 1100 °C at a rate of 5 K min^{-1}, followed by soaking for 2 h. The resultant carbons CEL-95, CEL-100, CEL-105 and CEL-110, were ground to the particle size of <20 μm. For coating with pyrolytic carbon (CVD), the powders, placed in a quartz boat, were heated in the mixture of 10 vol% of methane in nitrogen at 830 °C for times ranging from 0.5 h to 2 h. The symbols of PC coated carbons were created by adding CVD duration time after slash (e.g. CEL-100/1.5).

2.2. Structural and textural characterization

The carbons were characterized in terms of chemical composition, structural arrangement (XRD), morphology (SEM) and microporosity development.

CHNS contents were determined using the elemental analyzer CHNS VARIO EL (Elementar Analysensysteme GmbH). The oxygen content was measured directly on the Carlo Erba analyzer. The particle morphology of carbons were assessed by scanning electron microscopy (Zeiss EVO LS15).

X-ray diffraction measurements were performed on Rigaku powder diffractometer ULTIMA IV using Cukα radiation ($\lambda=0.15406$ nm) and 40 kV accelerating voltage. The structural parameters calculated from the XRD spectra included the interlayer distance d_{002} and crystallite height L_c and diameter L_a. L_c and L_a values were calculated from the width at the half-maximum of 002 and 10 bands, respectively, using the Scherrer equation [22].

The porous texture was characterized by the adsorption of nitrogen at 77 K (ASAP2020, Micromeritics) and carbon dioxide at 273 K (NOVA 2200, Quantachrome). Before measuring the samples were degassed overnight at 300 °C. N_2 adsorption isotherms were used to determine the total micro- and mesopore volume V_T, micropore volume V_{DR} from the Dubinin–Radushkevich equation [23]. The QSDFT analysis [24] was applied to N_2 adsorption isotherms obtained using ASAP to determine pore size distribution (PSD) and surface area S_{QSDFT}.

CO_2 adsorption isotherms at low pressure <10 kPa are assumed to correspond to the adsorption in ultramicropores, i.e. narrow micropores of size <0.7 nm. The isotherms were used for the calculation of the ultramicropore volume V_{DRCO2}. The DFT method was applied to the CO_2 adsorption isotherms to determine the ultramicropore size distribution.

2.3. Electrochemical measurements

Electrochemical tests were performed in a coin-type cell (CR2032, Hohsen Corp. Japan). Half-cell was assembled with carbon electrode as an anode and metallic lithium foil as a cathode and reference electrode. Electrolyte used was 1 M solution of lithium hexafluorophosphate ($LiPF_6$) in a mixed solvent: EC: DMC, 1:1 by volume. A glass microfiber separator (Whatman, GF/F, thickness of 420 μm) wetted with the electrolyte, was sandwiched between the carbon electrode and Li foil. To avoid any possible side effects which could influence on the lithium insertion/deinsertion behavior, the parameters of the electrode and the test conditions were normalized. The electrodes of 6–8 mg mass, 14 mm diameter and 100 μm thick were pressed from a mixture of active material (85%), PVDF binder (10%) and conducting carbon black (5%).

Full-cell was assembled with double-side coated electrodes. The cathode was manufactured from commercial $LiNiCoMnO_2$ (NMC) powder of 5:3:2 atomic ratio (MTI Corp., USA) coated on Al foil using the same percentage of binder and carbon black as for anode. The electrodes were stacked inside the CR2032 cell with a trilayer PP/PE/PP separator (MTI Corp., USA, thickness of 25 μm). As an electrolyte was applied 1 M $LiPF_6$ in EC+DMC with 10% addition of fluoroethylene carbonate (FEC).

The standard test of the assembled lithium/carbon half-cell comprised discharging from the rest potential to 0.005 V versus Li, and 50 full cycles between 0.005 and 1.5 V. Two different charging/discharging modes were used in the tests. In the conventional constant current (CC) mode the cell was charged and discharged at $C/20$, where C corresponds to the theoretical capacity of graphite (372 mA h g^{-1}). Alternatively, the lithium insertion into carbon material (cell discharge) was performed using a constant current+constant voltage mode (CC+CV) with the current density set at $C/2+C/100$. The deinsertion occurred at a current density ranging from $C/5$ to 1 C. The galvanostatic characteristics of a cell were used to determine the total first discharge capacity (C_T), reversible capacity C_{rev} and irreversible capacity C_{irr}. Coulombic efficiency CE was defined as the ratio of deinsertion to insertion charge of the respective cycle. In some cases the efficiency of the first cycle (CE_1) and average value in the range of 2 and 50 cycle (CE_{EV}) were specified. The capacity corresponding to the low voltage plateau, i.e. below 40 mV (C_{LV}) was assessed from the second discharge cycle.

The laboratory made full-cell and reference commercial Li-ion cell (LIR2032, Batimex®) of nominal capacities (C^*) 50 and 40 mA h, respectively, were charged at $C^*/3+C^*/50$ and discharged at $C^*/2$ current.

All the measurements were performed at room temperature using multichannel potentiostat/galvanostat VMP3 (Biologic, France).

3. Results and discussion

3.1. Effect of carbonization temperature on the properties of cellulose-based carbons

Table 1 presents the chemical composition of cellulose-based

Download English Version:

https://daneshyari.com/en/article/7920873

Download Persian Version:

https://daneshyari.com/article/7920873

Daneshyari.com