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Hydrolysis lignin: Electrochemical properties of the organic cathode material for primary lithium battery

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ABSTRACT

Electrochemical energy production has been extensively used in large scale applications. At present, organic compounds are considered as efficient and environmentally friendly electrode materials. The paper describes the study of the possibility of using hydrolysis lignin as the lithium battery cathode material. Hydrolysis lignin features have been investigated by the impedance spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The discharge performance of hydrolysis lignin-based lithium battery was investigated at room temperature using 1 M $LiBF_4$ in γ-butyrolacton electrolyte system. It was found that the specific capacity of hydrolysis lignin was equal to 450 mAh g^{-1} at a discharge current density of 25 μA/cm^2. Two main voltage plateaus located at ~1.8 and ~1.1 V were observed. The chemical composition of cathode materials upon battery discharge down to 0.9 V was studied by the X-ray photoelectron spectroscopy and infrared spectroscopy. The suggestions on possible electrochemical reactions occurring in the lithium/hydrolysis lignin system were made on the basis of the products composition analysis. The results demonstrate the potential of hydrolysis lignin based batteries to be used as low-rate power sources.

1. Introduction

Recently, the energy source industry has been under intensive development. The electrochemical energy sources required for household, engineering, aerospace, medicine, and special equipment are being introduced into various fields of human activities on a large scale [1–3]. Numerous studies related to lithium batteries (LB) are focused on the increase of the specific capacity, in particular, through search and creation of novel electrochemical systems for both primary and secondary LB [4,5]. One of the topical and promising directions of research in the field of LB comprises the development of novel electrode materials based on organic compounds [6,8].

Recently, European researchers [9] have shown that lignosulfonate compounds are a promising organic electrode material for environmentally friendly secondary energy sources. However, fast self discharge was the problem of lignosulfonate-based systems. Application of lignin in primary LB was proposed by Russian scientists in parallel with the European researchers [10]. It has been demonstrated that lithium/lignin cell designed in the Institute of Chemistry of FEB RAS is characterized by high theoretical specific capacity and open circuit voltage (OCV) of 3.3 V.

In the present paper the possibility of application of hydrolysis lignin (HL) as energy storage material has been investigated in detail. The battery electrochemical performance of material in an organic electrolyte system versus Li electrode was evaluated. The discharge specific capacity and voltage were estimated. Electrochemical reactions between Li and HL were suggested in accordance with the X-ray photoelectron spectroscopy and infrared spectroscopy data.

2. Experimental

2.1. Sample preparation

To prepare the cathode material, hydrolysis lignin was ground in a ball mill down to a particle size of 30 μm and, thereafter, washed through centrifugation in distilled water. Total time of product washing was approximately 10–12 h. Every 40 min the precipitate was decanted, and then a new portion of distilled water was added, the mixture was thoroughly stirred and centrifuged repeatedly. Finally, yielded product was dried at 60 °C during 24 h.

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2.2. Physical characterization

The HL characterization by the methods of scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed on a S5500 high-resolution scanning electron microscope (Hitachi, Japan) and an EDX-800HS energy-dispersive X-ray spectrometer (Shimadzu, Japan), respectively.

The HL electroconductivity was determined by means of the method of impedance spectroscopy using an Impedance/Gain-phase analyzer SI 1260 system (Solartron, Great Britain).

To determine the chemical composition of cathode materials, X-ray photoelectron spectroscopy (XPS) measurements were carried out on a spectrometry complex for surface investigations (SPECS, Germany) based on a 150 mm hemispheric electrostatic energy analyzer. Prior to XPS analysis, electrodes were removed from the batteries within the dry glove box in the argon atmosphere. Then the electrodes were mounted into small glass cases in the glove box and transported to the analysis chamber. Finally, the material was moved into a XPS chamber in Ar flow during several seconds to avoid contamination from air. The electron excitation was performed using MgK_α-radiation. The calibration of the binding energy values was performed on C 1s lines of hydrocarbon electrons and O 1s and Si 2p lines of silica contained in the samples. To study the structural peculiarities of the passive layer formed as a result of interaction of HL and electrolyte, which was appropriately named solid electrolyte interphase (SEI), and deeper layers and to determine the chemical composition of the products of interaction between Li^+ and HL, the samples were gradually etched down to a depth of 300 Å by argon ions having an energy of 5000 eV at an etching rate of $\sim 10^{-1}$ Å s^{-1}.

Infrared (IR) absorption spectra were recorded on a Shimadzu IRAffinity-1 spectrophotometer (Shimadzu, Japan) in the range 400–4000 cm^{-1}. The cathode materials samples were prepared in the form of suspensions in Vaseline oil on KRS-5 substrates.

2.3. Electrochemical study

A standard STC-19 two-electrode cell (MTI, USA) was used to test the electrochemical performance of the hydrolysis lignin. The thickness of lithium metal disk anode was 0.1 mm. The cathode slurry was composed of 76 wt.% active component (HL powder), 11 wt.% polytetrafluoroethylene (PTFE)-based binder (F-4D suspension, Dalkhimia Ltd., Russia), and 13 wt.% carbon black to insure electronic conductivity (Lib-CGP MTI, USA). The components were weighed using an AUW120D analytical balance (Shimadzu, Japan) and mixed. Thereafter, the cathode paste was attached to a steel mesh current collector disk of a diameter of 13 mm. The working electrode was dried at 110 °C to remove traces of water with subsequent pressing between two steel plates at a pressure of 5 MPa. The final thermal treatment of the cathode was performed in a DZF-6020-110P vacuum furnace (MTI, USA) at 280 °C for 2 h. The weight of the active material (HL) was changed in the range from 80 to 90 mg. 1 M $LiBF_4$ in γ-butyrolacton was used as an electrolyte. To prevent short circuit, a polypropylene separator was placed between lithium anode and cathode. The cells were assembled in a dry glove box in the argon atmosphere. Relaxation of each system was performed for at least 12 h to stabilize the cell open-circuit voltage.

The investigation of the Li/HL cell was performed at room temperature using a Solartron Analytical Celltest System (Solartron, Great Britain), consisting from a 1470E potentiostat/galvanostat and a FRA 1455 frequency response analyzer. The parameters were measured by discharging at current densities of 25 and 75 μA cm^{-2}. The cut-off voltage U_{cov} was set at 0.9 V, which is a typical value of the final voltage of 1.5 V-elements applied in power supply of a number of advanced low-power devices and instruments [11]. The evolution of the Li/HL impedance was studied by the method of electrochemical impedance spectroscopy in the frequency range from 10 mHz up to 1 MHz. The initial impedance measurement was carried out at an open circuit potential of 3.3 V. To study the impedance behavior of the Li/HL system and the processes occurring in it, the discharge of the Li/HL was periodically stopped to record impedance spectra. Prior to the impedance experiments the cell was left to rest for up to half an hour in order to characterize the Li/HL system at equilibrium. All the spectra were recorded at room temperature. To obtain a reliable result, the measurements were carried out on at least three cells of the same type. The value of the standard fitting criterion χ^2 did not exceed 10^{-3} for all the spectra in the present work.

3. Results and discussion

3.1. Hydrolysis lignin morphology and composition

According to the SEM data, the HL particle size changes within the range from 5 up to 30 μm (Fig. 1a), whereas each particle has a developed system of micro- and macropores on its surface (Fig. 1b). Such HL morphological structure could facilitate to a substantial degree the diffusion of lithium cations in the cathode bulk during the lithium battery operation.

In accordance with the results obtained by the EDX method and the literature data (Table 1), HL contains, aside from main elements (C, H, and O), impurities (less than 5 wt.%) of, predominantly, Si and Na. According to [10], high oxygen content (about 23 wt.%) in the hydrolysis lignin composition asserts the possibility of its efficient application as cathode materials for primary LB. It is impossible to detect hydrogen using the EDX method. The typical hydrogen content in HL changes in the range from 5 up to 7 wt.% [12].

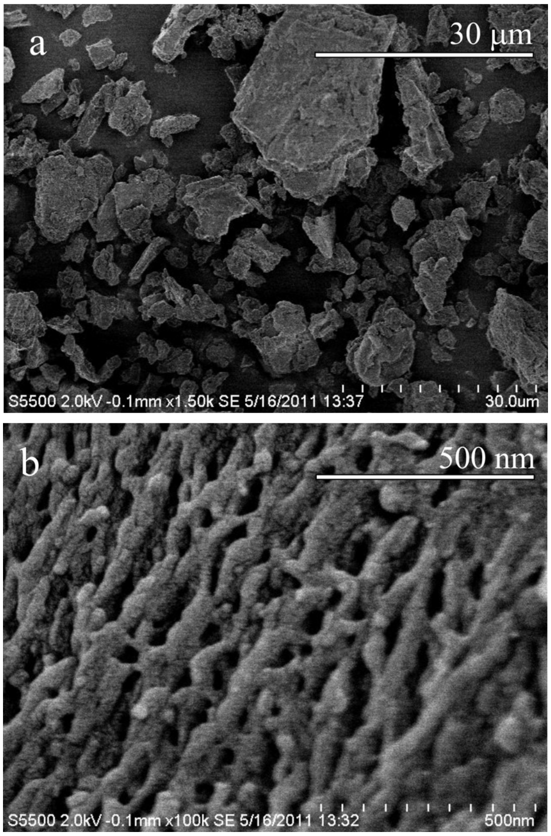

Fig. 1. SEM-images of hydrolysis lignin obtained at different resolutions.