

Electrochemical performance of Klason lignin as a low-cost cathode-active material for primary lithium battery

Sergey V Gnedenkova, Denis P Opra^{a*}, Ludmila A Zemnukhova^{a,c},
Sergey L Sinebryukhov^a, Iliya A Kedrinski^b, Olga V Patrusheva^c, Valentin I Sergienko^a

a. Institute of Chemistry, Far Eastern Branch, Russian Academy of Sciences, 100-Letiya Vladivostoka Pr. 159, Vladivostok 690022, Russia;

b. Siberian State Technological University, Mira Pr. 82, Krasnoyarsk 660049, Russia;

c. Far Eastern Federal University, Suhanova St. 8, Vladivostok 690091, Russia

[Manuscript received November 20, 2014; revised December 23, 2014]

Abstract

A few classes of organic compounds are promising electrode-active materials due to their high power and energy densities, low cost, environmental friendliness, and functionality. In the present work, the possibility of using Klason lignin extracted from buckwheat husks as a cathode-active material for a primary lithium battery has been investigated for the first time. The reaction mechanism in the lithium/lignin electrochemical cell was suggested based on the deep galvanostatic discharge (up to 0.005 V) data and cyclic voltammetry results. The dependence of the electrochemical behavior of the Klason lignin on the milling degree was evaluated. The maximum specific capacity of the lignin is equal to 600 mAh·g⁻¹ at a discharge current density of 75 μA·cm⁻². Beneficial effect of the thermal treatment of the Klason lignin cathode at 250 °C on the cell performance was established. It was found that the discharge capacity of the cell increased by 30% in the range from 3.3 to 0.9 V for the treated cathode material. These results demonstrate the prospects of using Klason lignin-based electrochemical cells as low-rate primary power sources.

Key words

Klason lignin; primary lithium battery; organic electrode; buckwheat husks

1. Introduction

Electrochemical energy sources have been long used for power supplies in numerous applications. Lithium batteries with inorganic cathode materials are widespread energy sources for high-technology equipment due to their excellent performance [1–3]. However, conventional electrochemical systems are characterized by significant limitations of their component base because of natural resources exhaustibility and their absence of renewability. In addition, mining operations cause CO₂ emissions (70–100 kg per 1 kWh of energy) [4,5]. Ecological policies of the developed countries are presently stimulating the growth of interest in materials synthesized by low-cost and environmentally friendly processes.

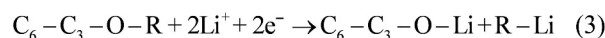
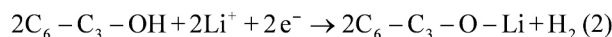
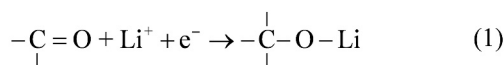
Organic compounds comprise an alternative class of electrode materials. Environmentally friendly synthesis of non-toxic organic compounds is a desirable way to design sustainable energy sources. Advanced organic electroactive ma-

terials can be classified into several groups: (a) conjugated polymers, (b) organosulfur compounds, (c) nitroxyl radicals, and (d) materials containing chemically active C=O groups [6–11]. Electroactive redox properties of organic materials have been under intensive investigation since the 1990s. To date, a number of organic compounds have been synthesized; a large knowledge base about fundamental processes in the organic lithium batteries has been accumulated; and some practical devices have been developed, for example, the organic radical battery invented by the NEC Corporation [12]. However, state-of-the-art organic lithium batteries suffer from grave disadvantages such as low practical-specific capacity, dissolution of the compounds into the electrolytes, limited discharge voltage [4,13,14]. Therefore, promising organic compounds for both anodes and cathodes must be found in order to design high-performance sustainable lithium batteries.

Recently, researchers [15,16] showed that lignosulfonate compounds are promising organic cathode materials for sustainable electrochemical energy sources. The possibility

* Corresponding author. Tel: +7(423) 2311889; Fax: +7(423) 2312590; E-mail: ayacks@mail.ru

of using hydrolytic lignin as an environmentally friendly cathode-active material has been proposed [17–19]. According to the literature [15–18], the electrochemical reactions on a cathode during lithium/lignin cell discharge occur between Li^+ ions and different oxygen-containing groups of lignin.



where (C_6-C_3) is the phenylpropane structural unit of lignin, and R is (C_6-C_3) or CH_3 .

Researchers have investigated the electrochemical behavior of lignin derivatives as anodes for lithium batteries [20–22]. The lignin's strong points include vast availability, renewability, and low cost. However, the basis of the suggested approaches consists if using industrial lignin, which is a byproduct of the chemical treatment of raw wood materials. Note that composition, structure, morphology, and other properties of industrial lignin strongly depend on precursors and technological conditions. The reproducibility of production processes and standardization of physicochemical properties are important points of lignin use as an electrode-active material for lithium batteries.

Although renewed large-tonnage plant wastes from cereal crop treatment are effective sources of unitized lignin, the knowledge base associated with the electrochemistry of plant lignin is insufficient [23]. We investigated the electrochemical performance of Klason lignin (KL) extracted from buckwheat husks as a cathode material for a primary lithium battery, and estimated the possibility of using KL as an energy-storage material.

2. Experimental

2.1. Materials

Husks of buckwheat (*Fagopyrum Mill*) were used as a precursor (2012 harvest, Dalnerechensk, Russia) in the delignification process. The sample was sieved to obtain particle size no less than 2 mm, washed in distilled water, and dried in air. The adipose matter was scavenged by keeping the sample (20 g) in the solution (80 mL) of ethanol and toluol at a volume ratio of 1 : 1 for 24 h. The sample was also filtered through a Buchner funnel using a water-jet pump and flushed by the solution. Klason lignin was prepared according to the Komarov method [24,25]. The sample was treated in 72% solution (20 mL) of H_2SO_4 for 48 h, after which the distilled water (160 mL) was added. Then the solution was boiled for 1 h and cooled down. Finally, the product was filtered through a Buchner funnel using water-jet pump, flushed by distilled H_2O , and dried in air. The lignin yield was in the range of 33%–35% based on the precursor weight.

2.2. Characterization

The elemental analysis of Klason lignin by energy-dispersive X-ray spectroscopy (EDX) was performed on an EDX-800HS (Shimadzu, Japan) spectrometer. Infrared (IR) absorption spectra were recorded on a Spectrum BX II (Perkin Elmer, Germany) spectrophotometer in the range 400–4000 cm^{-1} . The sample was pressured to the pellet with potassium bromide. The KL microstructure characterization by scanning electron microscopy (SEM) was performed on a high-resolution S5500 microscope (Hitachi, Japan). The KL conductivity was determined by impedance spectroscopy using an Impedance/Gain-phase analyzer SI 1260 system (Solartron, Great Britain). Thermal analysis experiments were performed using a DTG-60H (Shimadzu, Japan) instrument. Samples were heated from room temperature to 500 °C in the rate of 2.5 °C·min⁻¹. The elemental analysis of the gas atmosphere in the discharged Li/KL cell was made with a GC-2010 gas chromatograph (Shimadzu, Japan) with a μTCD microkatharometer. Chromatographic separation was performed on a MOL Sieve 5A PLOT 30 m×0.32 mm I. D. column (Supelco-Sigma-Aldrich, USA).

2.3. Electrochemical tests

To prepare the cathode material, the Klason lignin was milled. The cathode slurry was composed of 75 wt% KL powder, 15 wt% carbon black to insure electronic conductivity, and 10 wt% polytetrafluoroethylene binder. The components were weighed using an AUW120D analytical balance (Shimadzu, Japan). Homogenization of the cathode slurry was carried out on SFM-4 mixer (MTI, USA) over 12 h at a rate of 70 rpm. Thereafter, the cathode paste was attached to a steel-mesh current-collector disc 13 mm in diameter. The working electrode was dried in a DZF-6020–110P furnace (MTI, USA) at 110 °C to remove traces of water and subsequently pressed between two steel plates at a pressure of 12 MPa. Additional heat treatment of the cathode was performed at 250 °C over 2 h. The weight of the active material (KL) was changed in the range of 80–90 mg.

A Swagelok-type two-electrode cell was used to test the electrochemical performance of the Li/KL system. The thickness of the lithium metal disc anode was 0.1 mm. The electrolyte was 1 M solution of LiBF_4 salt in γ -butyrolacton. To prevent a short-circuit, a polypropylene separator was placed between the lithium anode and the cathode. The cells were assembled in a dry glove box in argon atmosphere. Relaxation of each system was performed for at least 12 h to stabilize the cells open-circuit voltage (OCV).

The performance investigation of the lithium/lignin cell was done at room temperature with an Analytical Celltest System (Solartron, UK). The Li/KL operating parameters were measured by the galvanostatic discharge at a current density of 100 $\mu\text{A}\cdot\text{cm}^{-2}$ with the cut-off voltage set at 0.9 V, which is a typical value of the final voltage of primary 1.5 V-elements applied in the power supply of a number of up-to-date low-

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