NOVEL CARBON MATERIALS FOR BATTERY APPLICATION

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Introduction

Carbon based electrode materials represent the object for intensive investigations as from the point of view of the progress in the field of lithium ion accumulators, so in view of the development of technological applications of fibrous carbon. We studied methods of obtaining, structure and characteristics of new carbon materials with the aim to use them as electrode materials for chemical current sources. The obtained results confirm that electrodes, prepared with the method, proposed by the authors, are perspective and allow obtaining high values of energy density and capacity in comparison with standard electrodes. This work is aimed at study of cathode and anode characteristics of new carbon materials in lithium chemical current sources. Rapid increase of mobile facilities market: cell phones, portable computers, diminutive record-players, digital cameras, watches, etc. led to increased rush of compact energy sources. At the same time electrochemical elements and accumulators, i.e. chemical current sources are beyond comparison. Chemical current sources with lithium anode take first place among self-contained power supply facilities, gradually replacing less effective traditional current sources of zink - manganese dioxide systems. Lithium ion batteries (LIB) are leading path for portable power sources for different applications. The leading role of LIB based on its excellent power density and voltage characteristics.

Increased shift of the coefficient of cathode material application is the general problem of producing of elements of lithium – liquid oxidant system [1]. Processes of oxidant reduction at porous cathode are determined by the structure and characteristics of using for their production electrographite materials. One of the ways of rise of discharge characteristics is obtaining of fibrous carbon based cathode materials. Recently, carbon materials specialists pay attention to the process of catalytic cracking of hydrocarbons. Carbon precipitations on dispersed metal particles occur as the result of catalytic reaction. These precipitations have specific forms and characteristics, which allow considering them as perspective ultradispersed systems using in various fields of chemistry. [2, 3]. At present, intensive researches are carried out in this direction, which determined that improvement of effectiveness depends on such characteristics as specific surface, porosity and electroconductivity of carbon materials. Among developing power-consuming lithium electrochemical elements thyonilchloride is one of the most perspective. Its theoretical energy density is 1200 Vt.h/kg. However, in practice potential capabilities of this system are half-realized at best. In practice, a soot cathode with the “sphere layers” structure is realized and used in industrial production of thyonilchloride electrochemical element. Requirements, demanding of cathode, are realized with essential restrictions. The presence of connective in interstice makes difficult for electrolyte migration and lowers its characteristics. In cathode with the “felt” type structure requirements for electroconductivity are realized with restriction (electric contacts inside the layer are dotty and strength is high). Nevertheless, such structure has a good permettivity for electrolyte and cathode has a developed surface.

Among available lithium ion batteries (LIB) are the most perspective. Developed by Japanese researchers Li carbon (LiC6) is used as anode material [4-7]. Although many kinds of carbonaceous materials have been tested as anodes for LIB [8], natural and synthetic graphite materials are used as practical anode materials for LIBs, because this material has specific capacity of 372 mAh g^{-1}, and exhibits good reversibility and flat discharge profiles. Propylene carbonate (PC) based electrolyte solutions are attractive because of their superior ionic conductivity at ambient temperatures [9]. However, graphite has poor compatibility with PC based electrolytes due to solvent co-intercalation phenomena, which leads to exfoliation of the electrode structure. Therefore, the seeking of novel anode materials with enhanced cycling performances and good compatibility with PC electrolyte solution is crucial. In present work we report experimental data on preparation, characterization and electrochemical tests of carbon obtained from apricot stone as anode for lithium ion batteries.

Experimental

Cathode was formed by growing of the layer of fibrous carbon at a shunt – nickel mesh. В качестве катализатора использовали соли никеля. Nickel mesh, treated by catalyst, was placed into reactor, and after gas flow and temperature were set, overcarbonization process was realized during some hours. Propane served as carbon source. After completing of the experiment obtained product was weighed and mass increase was calculated by time and given temperature. Solid phases samples, obtained in reactions, were investigated by physical methods.
Carbonization of apricot stone samples (AS) was carried out in isothermal conditions in inert gas flow at temperature 300-900^{o}C; the argon flow rate was 50 cm^3 min^{-1}. The fractions of AS with diameters of d=2 mm, 4 mm, 6 mm were placed in a reactor. Specific surface area determination was carried out with thermal desorption method. The thermal properties of the system were estimated via differential thermal analysis method (TGD9600, Sinku-rico) at a scanning rate of 10°C min^{-1} in N_2 and air atmosphere.

The electrochemical measurements were carried out with the use of a CR2032 coin-type cell. Li metal was as a counter electrode and comparison electrode. The cells were galvonastatically cycled between 2.50 and 0.01 V *vs.* Li/Li^+ at 30°C on Hokuto Denko charge-discharge tester at various current densities.

Results and Discussion

Fig.1 shows a discharge curve for nickel mesh with a “thin” and “thick” blanket of fibrous carbon. Disruption voltage especially at initial time is severely higher. Already in these conditions one can say about commensurable values of capacities, and accordingly, about high values of energy density for electrode, prepared by metal overcarbonization, in comparison with prepared by traditional technologies.

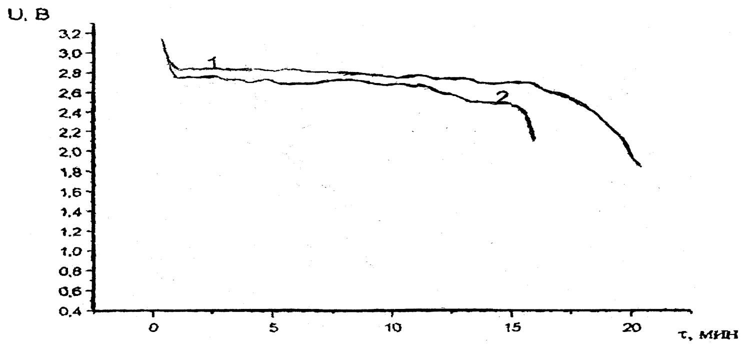

Fig. 1. Discharge characteristics of nickel-carbon cathode
1 – superficial overcarbonization, i = 5 мA/sm^2
2 – full overcarbonization, i = 10 мA/sm^2

In our study we attempted to prepared anode using carbonized apricot stone. The samples carbonized at 750^{o}C were used for anode preparation after purifying by isopropanol and drying at 110^{o}C for 12 hours in vacuum oven. The half cell tests were carried out using different electrolytes at room temperature. Fig. 2 shows the cycling data for the mentioned cells at different cycling rates and with different electrolytes. It can be seen that the carbonized apricot shell showed an excellent stability as an anode in electrolytes including various salts and solvents at high cycling rates.

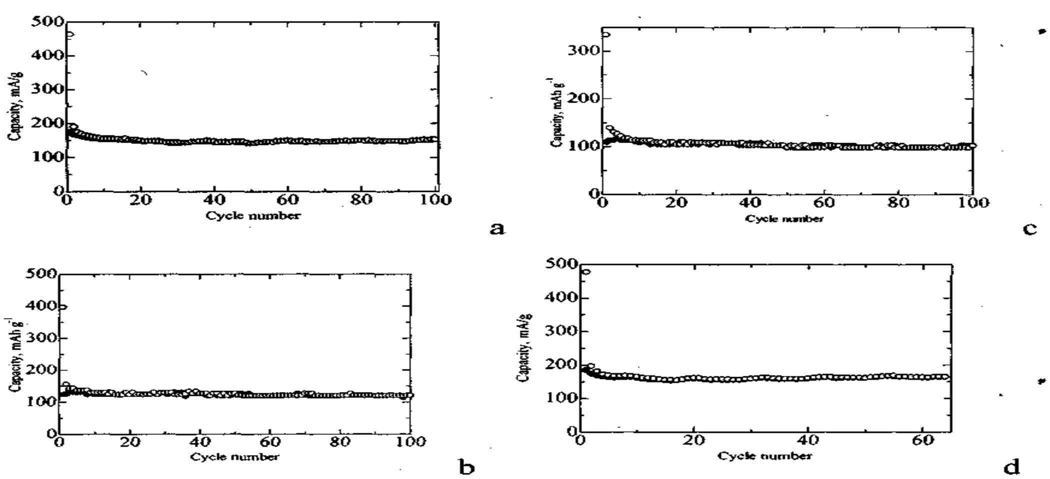

Fig. 2. Cycling performances of Li/1 mol l-1 LiClO4 in EC:DEC=1:1/ABR
(a) 1C; (b) 2C; (c) 3C (d) LiPF6, 1C

Conclusions

1. The method of overcarbonization of nickel mesh by catalytic pyrolysis with fibrous carbon formation was developed. Processes of formation of fibrous carbon layers were studied depending on experiment condition and optimal conditions for overcarbonization are found.
2. The method of carbonization of apricot stones was developed and optimal temperature of the process was found.
3. Models of chemical current sources were tested on the base of the lithium – chloride thyonil system using obtained graphite materials as cathode. Specific characteristics of proposed cathodes in many cases essentially exceed specific characteristics of cathodes produced with traditional methods.
4. Electrochemical tests of the material, obtained from carbonized apricot stones as anode in coin-type cells using galvanostatic method of cycling were carried out. It was showed that carbonized apricot stone as anode in used electrolytes, including different salts and solvents, shows excellent stability at high values of cycling.

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