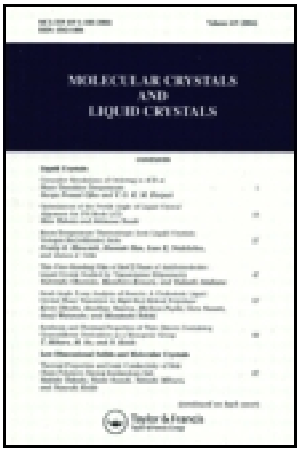

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Electrochemical Properties of Lithiated Carbons

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The degree of reversible and irreversible insertion of lithium in the fibrous carbonaceous materials was estimated by charge-discharge characteristics. The electrochemical storage of lithium ions, i.e. specific capacity, widely ranged from 100 to 700 mAh/g depending on the textural properties and chemical composition of carbons. The elucidation of irreversible loss of capacity was undertaken for carbons obtained from different precursors and prepared in a wide range of temperatures. Especially, the role of heteroatoms in the process of lithium insertion was considered for carbons prepared at temperatures from 600°C to 1000°C. The value of electrochemical potentials for lithiated carbons, more or less close to the potential of metallic lithium, is influenced by the stoichiometry of the compound and the way of Li-C bonding. Some carbons pointed out a large hysteresis, i.e. a high divergence between average discharge and charge potential. The reversibility of lithium insertion was also investigated by the potentiodynamic technique.

Keywords: lithium-ion cells; lithium intercalation; carbon fibrous felts

INTRODUCTION

Rechargeable battery market for portable electronic devices (notebooks type PC, wireless phones, camcorders) has a strong tendency to expansion [1]. Lithium-ion cells based on carbon anodes fulfil such requirements of safe and up-to-date accumulators with a profitable energy density (150 Wh/kg) and a high voltage (3-4 V). Carbons with controlled structural and textural properties are the most promising materials as a host for lithium ions[2]. The capacity of the carbon electrodes for lithium insertion is mainly dependent on the nature of the carbon, i.e. structure, texture, composition but also on the electrolyte used. However, the mechanism of lithium storage into carbon materials as well as reversibility and irreversibility of this process is not yet fully elucidated.

In the present work various kinds of carbon fibres have been applied as anode materials for secondary lithium-ion cells. Especially from construction point of view, carbon felts seem to be very attractive for assembling the cells. The aim of investigations was an electrochemical characterisation of such fibrous felts for elucidation a mechanism of the reversible insertion of lithium ions.

EXPERIMENTAL

For the electrochemical investigations, lithium-carbon cells of CR 2016 type were assembled in the Central Laboratory of Accumulators and Cells (Poznan). Some experiments were performed in a laboratory cell. Carbon fibrous felts obtained from different precursors, i.e. cellulose (10N), polyacrylonitrile (11N, 122, 28, B2) and wool (12N) were provided by Carbon Institute (Raciborz-Poland) and Sigri (Germany). Electrodes from a carbon felt were cut directly in the shape of disk with diameter of 14.2 mm. Depending on the felt density the weight ranged from 16 to 60 mg. Prepared carbon electrodes were dried in the inert atmosphere at 150^{0}C during 16 hours.

A mixture of ethylene carbonate (EC) + diethylcarbonate (DEC) with 1 M of $LiClO_4$ was mainly used as an electrolyte and only in some cases propylene carbonate (PC) + 1,2-dimethoxyethane (DME) with 1 M of $LiClO_4$ played this role. Before usage the electrolyte was carefully dried by lithium molecular sieves. The content of water measured by a Karl-Fisher method did not exceed 15 ppm. The amount of electrolyte in the button cell was about 0.2 ml.

Separator Celgard®2500 (Hoechst-Celanese, Charlotte NC) fulfiled a dendritostatic role between anode and cathode during charge-discharge cycles.

For the galvanostatic and potentiodynamic experiments potentiostat Elpan EP 20A and generator EG-20 were used.

RESULTS AND DISCUSSION

Host materials for lithium insertion were selected from different carbon fibreous felts. Carbon fibres as felts are a very attractive material because electrode could be easily prepared in the shape of disk for button cells (by cutting) or in the rolled version which might be used for cylindrical construction of cells with a high energy density. Temperature for carbonisation of felts was ranged from 600°C to 1100°C, but 800^{0}C was a minimum for thermal treatment to obtain a sufficient conductive matrix. Average specific resistivity for investigated felts was 15 to 50 Ωcm at room temperature. Morphology of carbon felts differed depending on the precursor and technology of preparation. Example of polyacrylonitrile fibre felt of 28 PAN type is shown in the Scanning Electron Microscopy (SEM) photographs (Fig. 1). The diameter of fibres is ~13 μm and the cross section of a single fibre is an irregular circle. Polyacrylonitrile felts were characterised by BET surface area (14 - 17 m^2/g) evaluated by argon sorption at 77 K. Volume porosity of felts was ~94%.

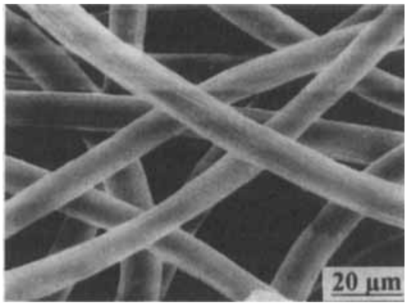

FIGURE 1 SEM photograph of polyacrylonitrile fibre felt (28 PAN)

For the electrochemical characterisation, the specific capacity (mAh/g) of various kinds of carbon felts was evaluated by the galvanostatic reduction. The value of 372 mAh/g has been obtained for pure graphite and corresponds to LiC_6 compound[5]. Galvanostatic reduction and oxidation of carbon felt (28 PAN) is presented in Fig. 2. Specific capacity during reduction of this felt is equal to 436 mAh/g and reversible capacity estimated from oxidation process is 306 mAh/g. These characteristics present a low hysteresis, i.e. overpotential for insertion and deinsertion of lithium ions is very comparable and during the reversion of current polarisation the potential drop is almost negligible. Generally, the polyacrylonitrile felts pointed out an insertion capacity during the first cycle in the range from 400 to 650 mAh/g and a reversible capacity of about 300 mAh/g. Elemental analysis of polyacrylonitrile felts (Raciborz) carbonised at 800°C was the following 92.60°/$_w$ of C; 4.52°/$_w$ of N; 0.53°/$_w$ of H.

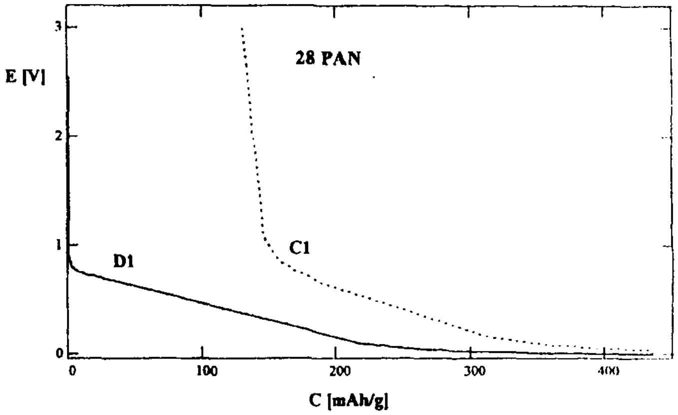

FIGURE 2 Discharge-charge characteristics of carbon electrode from polyacrylonitrile felt (28PAN -Raciborz). Electrolyte EC+DEC (1M $LiClO_4$)

Among all the investigated carbon felts, the lowest specific capacity i.e. 153 mAh/g for reduction and only 78 mAh/g for reversible capacity, was measured for the felt from cellulose precursor (10 N). Taking into account the elemental analysis of this felt (93.5°/$_w$ of C; 0.8°/$_w$ of N; 0.58°/$_w$ of H) it is remarkable that nitrogen content is very low. The degree of lithium sorption was definitively higher for the felt from carbonised wool (390 mAh/g), however, the irreversibility of this process is very high. The charge of 240 mAh/g is consumed for the formation of solid electrolyte interface layer and for the decomposition of electrolyte. In this case percentage of elements was 86.00°/$_w$ of C; 3.50°/$_w$ of N; 0.70°/$_w$ of H.

For better understanding the electrochemical behaviour of lithiated carbons, the process of lithium intercalation was investigated potentiodynamically for all the fibrous electrodes. Potential was varied from 3 V to 0 V vs Li/Li^+ with a scan rate of 1 mV/s. Analysis of potentiodynamic investigations pointed out a strong correlation between the shape of voltammograms and the reversibility of lithium insertion determined by galvanostatic method. During the first cycle two cathodic peaks were remarkable, the first one (between 2.5 V and 2.0 V) responsible for reduction of some oxygen traces and the second one (between 0.9 V and 0.5 V) connected with the reduction of solvent DEC or EC (Fig. 3). These two peaks are existing only during the first cycle and they do not have responses on the anodic side that clearly proves their irreversible character.

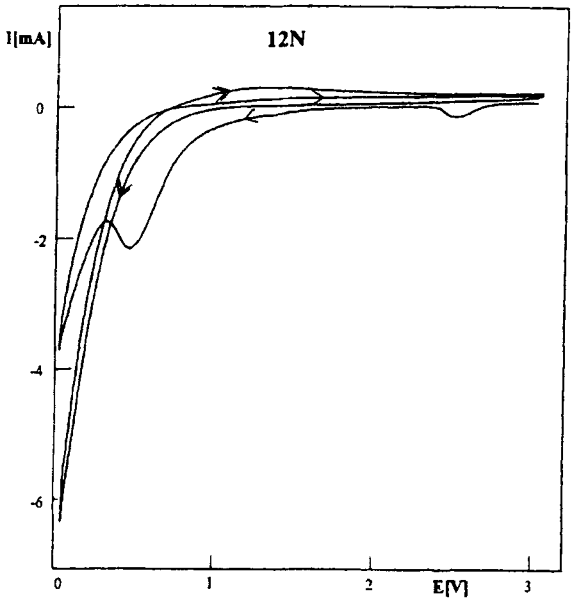

FIGURE 3 Voltammograms of carbon felt from wool (12N Sigri). Scan rate 1mV/s. Electrolyte EC+DEC (1M $LiClO_4$)

The strong increase of current below 0.5 V is strictly connected with lithium intercalation. The higher value of current (charge) in this region the higher capacity for lithium intercalation. During the reverse cycling of the electrode, i.e. from 0 V to 3 V, the anodic response is noted depending on the amount of inserted lithium during reduction. Fig. 4 presents two subsequent cycles for carbon electrode from PAN 28. From galvanostatic experiments this electrode pointed out a very limited irreversible capacity (100 mAh/g) and reversible capacity was 300 mAh/g. It is a reason why during the first cycle the peak connected with decomposition of electrolyte, i.e. irreversible process does not exist. In this case, on the anodic side, deinsertion process is well visible in the region from 0.5 V to 1.1 V, especially during the second cycle. The shape and the position of this anodic response is connected with a presence or a lack of hysteresis in a typical charge-discharge characteristics. The greater shift to anodic values the bigger hysteresis. It seems that the voltammetric method can give a very quick information about the Li insertion process.

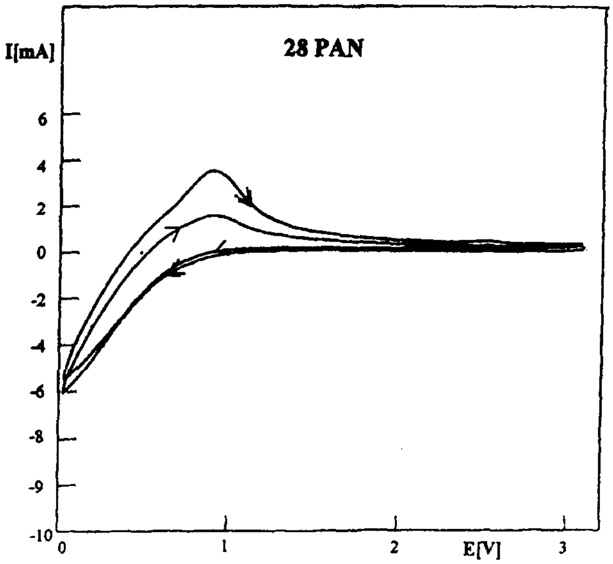

FIGURE 4 Voltammograms of carbon felt from polyacrylonitrile 28 PAN (Raciborz). Scan rate 1 mV/s. Electrolyte EC+DEC (1M $LiClO_4$)

Analysis of electrochemical potential for different lithiated carbons (without load) pointed out that the lower value of this potential the higher specific capacity. It seems that the kind of Li bonding with the host material is responsible for the value of potential and for the reversibility. The kind of lithium bonding will depend on the global electronic properties of host. In the case of nitrogen presence, substitutional N in carbon host will act as an electron donor (five valence electrons). It seems that Li-host bond will become weaken and the average voltage of lithiated carbon will decrease[2]. For the carbons which contain significant amount of heteroatoms, lithium ions could be electrostatically attracted or exchanged with surface functional groups due to the negative charge of carbon which will be strictly determined by composition (heteroatoms) and by external polarization. In such a case potential of lithiated carbon without polarisation easily shifts to more positive values. During lithium deintercalation, i.e. oxidation of carbon, due to the repulsion forces a part of lithium ions can be more or less easily expelled.

One can assume that through the controlled amount of heteroatoms it is possible to determine and control the electrochemical behavior of carbon materials during lithium insertion. Apart from nitrogen the strong effect of oxygen was also predicted and confirmed[4].

CONCLUSIONS

Among the various materials obtained from different organic precursors, PAN fibrous felt was the best host for lithium insertion. From galvanostatic and potentiodynamic investigations of carbon felts a good correlation was found between the character of voltammogram and the reversible capacity of lithium intercalation. For the first time, cyclic voltammetry performed on Li-carbon cells was used for elucidation of all the reduction and oxidation processes proceeding during electrochemical polarization from 3 V to 0 V. The well defined peak of current noted between 0.9 V and 0.4 V is connected with a solvent reduction followed by formation of protective passivating layer. Existence of this peak solely in the first cycle and the lack of anodic response for it, clearly proves the irreversible character of this process. In the case of a high reversible Li insertion, anodic deintercalation of Li is well remarkable on the voltammogram in the potential region from 0.5 V to 1.1 V. Electrochemical behavior of lithiated carbons, i.e. specific capacity, degree of reversibility and charge-discharge hysteresis, is strongly dependent on the textural and electronic properties of carbon host determined by the presence of nitrogen.

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