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Elzbieta Frackowiak [a]

[a] Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, ul. Piotrowo 3, 60-965, Poznan, Poland

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Carbon Fluoride Cathode Modified by Electroconducting Polymers

ELZBIETA FRACKOWIAK
Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, ul. Piotrowo 3, 60-965 Poznan, Poland

Carbon fluoride with a general formula $(CF_x)_n$ represents an attractive cathode material for primary lithium cells operating in aprotic medium. $(CF_x)_n$ compound was obtained by the gaseous fluorination of carbon tissue at 450 ^{0}C. The degree of fluorination, i.e. the value x for the final product, was equal to 0.95. During the electrochemical reduction of carbon fluoride, a ternary intercalated compound CLi_xF is formed which is chemically decomposed to carbon and lithium fluoride. Reduction process of $(CF_x)_n$ is irreversible due to covalent C-F bonding with sp^3 hybridization. This discharge process was strictly controlled by diffusion of Li^+ into the layered host of carbon fluoride. X-ray method was applied for elucidation of reduction process.
Modification of carbon fluoride was realized by using a composite material with different percentages of conducting organic polymer, i.e. polyaniline (PANI) in the form of emeraldine base (EB). PANI was introduced into the fluoride cathode material by a careful powder mixing or by the solution casting method using N-methylpyrrolidone (NMP) as a solvent. Electrochemical properties and kinetic parameters of composite $(CF_x)_n$ - PANI cathode were evaluated.

Keywords: carbon fluoride; lithium cell; polyaniline

INTRODUCTION

Carbon fluorides obtained at high temperatures, i.e. HT-CF compounds are very useful cathode materials for application in primary lithium cells[1-3]. The layered compound consists of distorted graphene layers with perpendicularly connected fluorine atoms. Covalent C-F bonding with C in sp^3 hybridization are fully responsible for irreversible reduction process[4].

The purpose of performed investigations is to better elucidate $(CF_x)_n$ reduction by using potentiodynamic and X-ray technique. Trials were also undertaken to modify the cathode performance through the addition of conducting polymer (PANI) in different percentage amounts from 25% to

100%. It is well known that PANI can be directly applied as a cathodic material in lithium batteries[5] or can be incorporated into transition oxide materials used as positive electrodes[6]. However, such cells cannot be loaded at high rate. In this work the influence of PANI additive on the reduction process of carbon fluoride electrode was estimated by different techniques.

EXPERIMENTAL

The highly fluorinated $(CF_x)_n$ was obtained by the gaseous fluorination of carbon tissue at 450 ^{0}C. The carbon tissue was formerly prepared from an organic viscose precursor through partial graphitization. The fluorination degree of polycarbonfluoride, i.e. the x value in the formula $(CF_x)_n$ was 0.9 to 0.95. Elemental analysis of this compound was performed. The value of n which characterises the polymerisation process was about 3500. The obtained carbon fluoride of light greyish colour possesses a very limited conductivity. For a better characterisation of this compound, a particle size and BET surface area (376 m^2/g) was measured by ASAP 2010. Scanning electron microscopy was used for the observation of the fibrous structure of carbon tissue before and after fluorination (Fig.1).

For the preparation of cathode material, a 4% amount of binder (PTFE) was used to obtain a homogeneous integrity of electrode. The improvement of conductivity was realized by addition of acetylene black (5%) and super fine colloidal graphite (5%). For modification of cathode material by electroconducting polymer, i.e. PANI, carbon fluoride was mixed with emeraldine base (EB) powder. EB was prepared chemically through the controlled oxidation of aniline solution (0.5 M) in hydrochloric acid (1 M) by ammonium persulfate. After vacuum drying EB was carefully milled. Several compositions of cathode material were prepared, i.e. $(CF_x)_n$ with 0%, 25%, 50%, 75% and 100% of EB. The amount of cathode material was equal to 100 mg, i.e. 86 mg $(CF_x)_n$; 4 mg PTFE; 5 mg acetylene black and 5 mg graphite. The composition of $(CF_x)_n$ with 25 % of EB was realized by carefully mixing 100 mg cathode material with 25 mg of EB. In such a way, all the mixed compositions were consisted of the same quantity of $(CF_x)_n$ material. From these thoroughly mixed materials the cathode pellets were pressed and after drying, the lithium cells of BR 2016 type were assembled in the glove box. For comparison, a few fluoride cathodes were covered by a solution casting film of EB in NMP solvent. The geometric surface area of all the used cathodes was 1.6 cm^2.

The used organic solvent for lithium perchlorate (1M) was a mixture of PC (propylene carbonate) and DME (1,2-dimethoxyethane) in the volume ratio (1:1). In some cases pure PC with 1 M $LiClO_4$ was used as electrolyte solution. Some experiments were also performed in a mixed solvent, i.e. EC (ethylene carbonate) + DEC (diethyl carbonate) with 1 M $LiClO_4$.

The prepared $Li/(CF_x)_n$ cells were investigated galvanostatically and potentiodynamically using potentiostat Elpan EP 20A, generator EG-20 and X-

Y recorder 4106. For the experiments at elevated temperatures, the conditions were controlled with an accuracy of 1 °C.

RESULTS AND DISCUSSION

The fibrous structure of carbon tissue obtained from a viscose precursor is shown in Fig.1a. After the fluorination process this structure is preserved (Fig.1b).

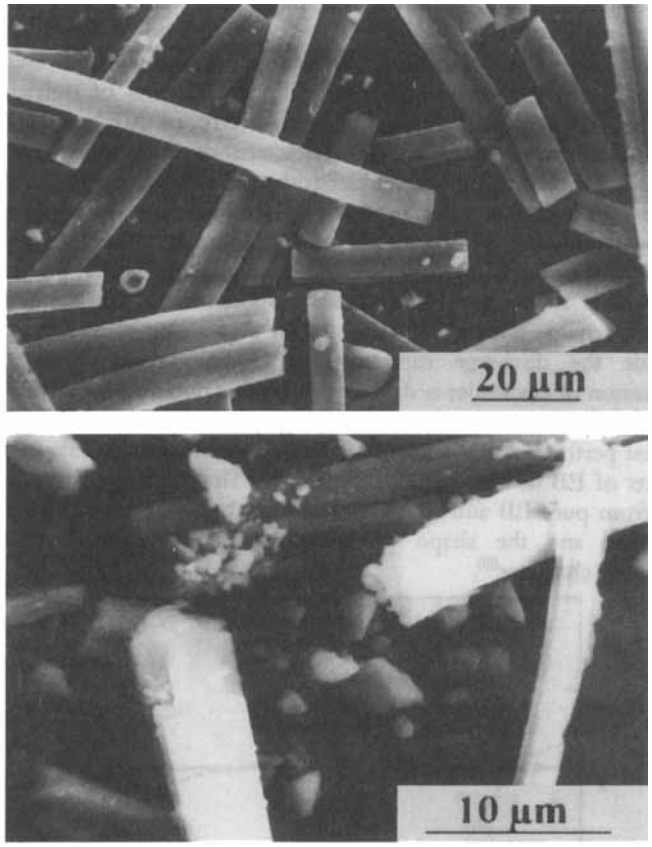

FIGURE 1 Carbon tissue a) before fluorination, b) after fluorination

During the discharge process of carbon fluoride cathode in $Li/(CF)_n$ cell, the following reaction of reduction takes place:

$$(CF)_n + n\,Li^+ + ne \rightarrow C_n + nLiF$$

The reaction is irreversible and lithium fluoride that is a non-soluble compound in aprotic medium easily precipitates in the layered $(CF)_n$ material. In fact, reaction proceeds through the unstable ternary compound CLi_xF [4] formed in the diffusion layer. The presence of a well crystallized LiF which amount gradually increased during reduction was already proved by X-ray method [7]. Formation of carbon during reduction causes an improvement of conductivity, hence, the flat discharge characteristic is observed for this system.

In the present work the influence of conducting PANI on the performance of $(CF_x)_n$ electrode was considered. Carbon fluoride electrodes modified by EB were discharged at the constant load of 1 mA (Fig. 2). The current value of 1 mA allowed to discharge electrodes with a strong load (0.65 mA/cm^2), the electrodes containing different amounts of polyaniline: 25%, 50%, 75%. For comparison pure cathode materials, i.e. $(CF_x)_n$ and EB were also investigated. From the discharge characteristics the capacity of cells was estimated. Theoretical capacity of electrodes with 86 mg of $(CF_x)_n$ is 74 mAh. In our case, 35 h discharge for pure $(CF_x)_n$ electrode gives 35 mAh, i.e. 47% of cathode utilization. For 25% additive of EB, 43 mAh capacity is observed, what gives 58% of cathode utilization. Due to the high load the first part of discharge characteristic shows a rapid decrease of potential for all the cells and the average discharge potential is about 2.2 V. Depending on the composition of electrode the discharge capacity differs significantly. However, even if composition of electrodes is different and redox potential for $(CF_x)_n$ and PANI is not exactly the same, only one discharge plateau is remarked in all the cases. The best performance is obtained for $(CF_x)_n$ electrode with 25% of EB. Larger amounts of EB do not bring better results. The discharge curve of electrode made from pure EB and $(CF_x)_n$ electrode with 75% additive of EB is almost overlapped and the shape of the discharge curve confirms a strongly capacitance character[8].

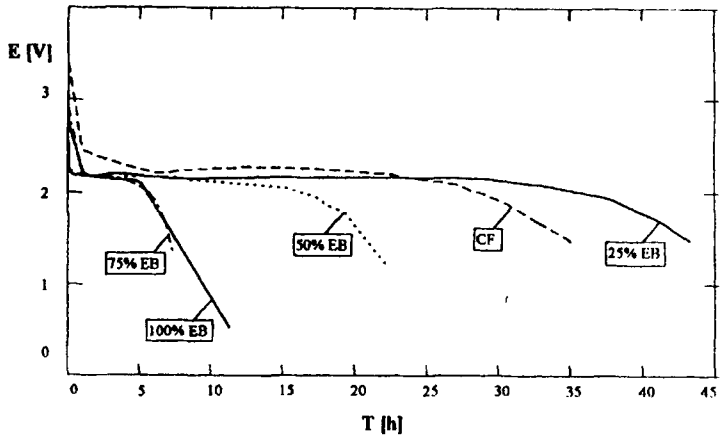

FIGURE 2 Discharge characteristics of $(CF_x)_n$ electrode (100 mg) with different additives of polyaniline (EB) at current of 1mA. S=1.6 cm^2.

For the determination of kinetic parameters for all the composite electrodes modified with EB an exchange current was estimated by the method of polarization curves taking logarithmic dependence of current vs. overpotential. For example, the value of exchange current for pure $(CF)_n$ electrode is 0.23 mA and for $(CF)_n$ electrode with 25% of EB is equal to 0.29 mA at 20°C. The higher the content of EB, the greater is the exchange current. For 50% of EB additive this i_0 value is 0.52 mA and for pure EB 0.58 mA. The experiments for estimation of exchange current i_0 have been also performed at elevated temperatures from 20°C to 120°C in order to investigate the kinetic parameters, e.g. activation energy. Dependence of exchange current on the activation energy is expressed by the following equation

$$\ln i_0 = \ln\Theta - E_a/RT$$

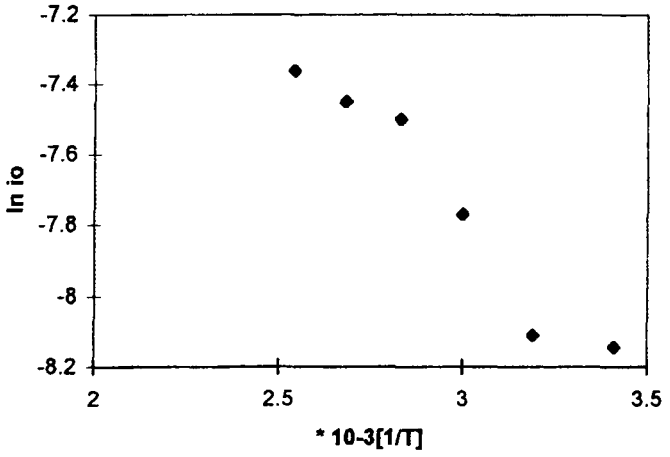

FIGURE 3 Dependence of exchange current ($\ln i_0$) versus temperature (1/T) for $(CF_x)_n$ electrode with 25 % of polyaniline (EB). S=1.6 cm^2.

One can deduce that exchange current increases exponentially when activation energy of electrode process decreases. From the dependence $\ln i_0 = f(1/T)$ the value of slope, i.e. activation energy of electrode process could be determined (Fig. 3). However, due to the fact that at low temperatures (20° to 40°C) the slope of the curves is different from that at high temperatures (60° to 120°C), it can be assumed that different processes dominate, depending on the temperature (e.g. Faraday reaction or diffusion). The low value of activation energy (3.3 kJ/mole for electrode with 25% of EB) can be the proof that diffusion plays a significant role in the reduction process.

Conclusions

The host layered structure of $(CF)_n$ is suitable for lithium insertion in reduction process that is diffusionally controlled. In order to improve the electronic properties of carbon fluoride, conductive polymer such as polyaniline has been incorporated to form a novel composite material. It is assumed that the presence of PANI chains with a high p-doping level could facilitate the insertion of lithium ions between the basal planes of lamellar $(CF)_n$ structure. Addition of PANI has a strong influence on the electrochemical behavior of cathodic material. Kinetic parameter, i.e. the value of exchange current, gradually increases with addition of EB from 0.29 mA for 25% to 0.58 mA for pure EB. Galvanostatic results confirm that among different cathodes, a composition with 25% addition of EB into cathode material enhances the utilization of $(CF)_n$ cathode. In this case electron and ion transport induced by incorporation of conducting polymer as well as redox capacity of PANI itself, provides a moderate increase of cell capacity. It can be also expected that the reversibility of this system will improve. It was clearly proved that the higher the amount of PANI the greater is the capacitance effect in discharge process because PANI is an active material for electrochemical capacitors. It seems that the content in the range lower than 25% until 50% of EB should be carefuly considered. The results confirmed some compatibility of polyaniline with fluoride cathode material.

Acknowledgments

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