

Electrochemical synthesis of lithium fullerides

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The electrochemical reaction of Li with fullerene in an aprotic electrolyte was studied. It was found that a lithium-rich fulleride with approximate formula $\text{Li}_{10}\text{C}_{60}$ can be obtained in the presence of a catalyst. This amount of Li is irreversibly incorporated into the structure. Additionally, 4-5 atoms can be introduced reversibly, thus allowing cycling the material with an initial reversible capacity of about $180 \text{ mAh}\cdot\text{g}^{-1}$. The pyrolysis product of a heterometal complex with monoaminoethanol ligands is shown to be a good catalyst for this process.

Fullerene / Lithium fulleride / Electrochemical synthesis

Introduction

Since the discovery of carbon allotrope fullerenes in 1985 [1], a large number of researches have been devoted to the chemistry of these substances. Many organic and inorganic derivatives have been obtained and their properties studied [2].

Among the inorganic compounds of fullerenes, the fullerides of alkali and alkali earth metals are of significant interest [3]. The alkali metal compounds of the fullerene C_{60} with composition Me_3C_{60} are the most studied ones because of their superconductivity below 30-50 K [4].

It is known that the outer surface of the spherical molecule C_{60} contains 12 pentagons and 20 hexagons [5]. Since a common graphene plane of graphite can accommodate up to 1 alkali metal atom per 1 of its 3 hexagons C_6 (which corresponds to the graphite intercalation compound MeC_6 [6]), one can expect the formation of metal-rich compounds of fullerene C_{60} with approximate composition Me_6C_{60} . Effectively, Me_6C_{60} compounds with *bcc* lattice have been obtained [7]. However, it was found that such metal-rich fullerides can be formed only with smaller (Li) atoms. Moreover, in the case of Li, further doping is possible, resulting in the formation of a product of composition $\text{Li}_{15}\text{C}_{60}$ with *fcc* packing of the fullerene ions [8]. The aim of this paper was to study the possibility of preparation of such Li-rich fullerides by the electrochemical method.

The cathodic reduction of Li^+ ions on a fullerene-based electrode under controlled current was chosen for this purpose. In some of the experiments, the electrode contained additives of a trinuclear complex compound of 2Co-Ni with aminoalcohol ligands, which, as shown earlier, possess electrocatalytic properties with regards to the reaction of Li intercalation into graphite [9,10].

Experimental

The fullerenes were obtained by the plasma arc method, which allows producing a large variety of carbon nanomaterials, as described in [11,12]. The sample selected for further investigations contained 85 wt.% of C_{60} , 14 wt.% of C_{70} , and about 1 wt.% of higher fullerenes.

The electrochemical reaction of Li with the fullerene was performed in a coin cell with a Li metal anode, 1M solution of LiPF_6 in an equimolar mixture of ethylene carbonate and methyl carbonate as the electrolyte, and a fullerene-based electrode as the cathode. The cathode mass contained 85 wt.% of the fullerene, 10 wt.% of carbon black (ABG-10) as the conductive additive and 5 wt.% of polyvinylidene fluoride (PVDF) as the binder. The experiments were carried out under galvanostatic conditions using a PC-governed power source with an operating current of $40\text{-}50 \text{ mA}\cdot\text{g}^{-1}$.

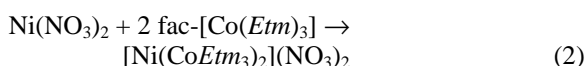
The catalyst, a heterometal 2Co-Ni compound with monoaminoethanol, was synthesized in two steps. First, an inner complex of Co(III) with aminoalcohol was obtained by means of the reaction of Co(II) nitrate with an aminoalcohol ligand in alkali ethanol medium in the presence of atmospheric oxygen according to the equation:



where $\text{Hetm} = \text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ (the notation Etm means the deprotonated form of Hetm , monoaminoethanol).

More details of the synthesis procedure can be found in [13-15]. Then polynuclear complexes were synthesized by reacting this complex with a solution of potassium nitrate in isopropanol for 3 days.

The chemical reaction of the formation of the trinuclear complexes can be written as follows:



Grafting of the complexes onto the surface of fullerene was performed by means of adsorption from an isopropanol solution. The time of treatment was 2 days, the content of complex in the solution was established to be 0.05 mole per 1 g of the sample. About 4.5 wt.% of the metals (2Co+Ni) were adsorbed under these conditions. After that, the samples were filtered and the product dried at room temperature.

Some samples were pyrolyzed in an atmosphere of pure argon for 1 h. The optimal temperature for the pyrolysis was established to be 500°C [10].

IR-spectra of the samples were taken on a Specord 75IR spectrometer in the range 400-4000 cm^{-1} , using tablets of KBr.

Results and discussion

Fig. 1 presents galvanostatic curves of the reduction of Li^+ ions on fullerenes in terms of the operating voltage vs. the number of Li atoms per 1 molecule of C_{60} .

As follows from the experimental data, less than 1 Li atom can be introduced into the structure of the fulleride if no catalyst is used (curve 1 of **Fig. 1**). Applying the 2Co-Ni complex compound as it is, that is, without subsequent thermal treatment (curve 2 of **Fig. 2**) made it possible to introduce about 4 Li atoms per C_{60} molecule. The electrochemical reaction is irreversible in both cases (that is, the Li atoms cannot be extracted by applying a reverse anodic current).

The reduction pattern differs significantly for the sample with the complex pyrolyzed at 500°C in argon atmosphere (curve 3 of **Fig. 1**). One can observe three distinct reduction steps: a – formation of Li_4C_{60} at ~1 V vs. Li; b – $\text{Li}_{10}\text{C}_{60}$ is formed at 0.75 V vs. Li and c – finally, the structure accommodates additional Li

up to approximately 16 atoms per C_{60} . This is in good agreement with the compositions obtained by a chemical method [8].

Fig. 2 shows IR-spectra of the initial sample (curve 1) and fullerene modified by the pyrolysis products of the heterometal complex compound (curve 2).

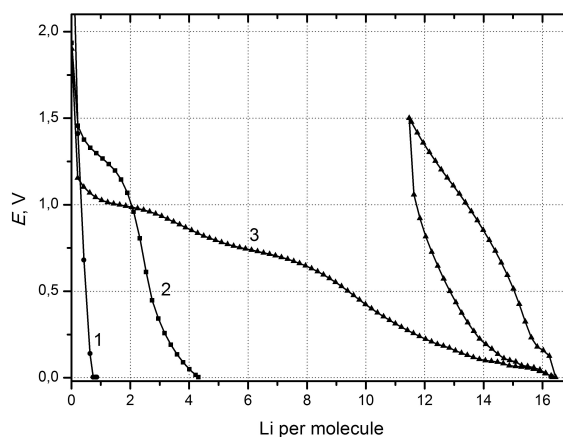


Fig. 1 Galvanostatic curves of Li^+ reduction on fullerene C_{60} at a specific current of $40 \text{ mA} \cdot \text{g}^{-1}$. 1 – initial sample; 2 – fullerene with grafted 2Co-Ni complex with monoethanol amine; 3 – the same with the complex pyrolyzed in argon at 500°C.

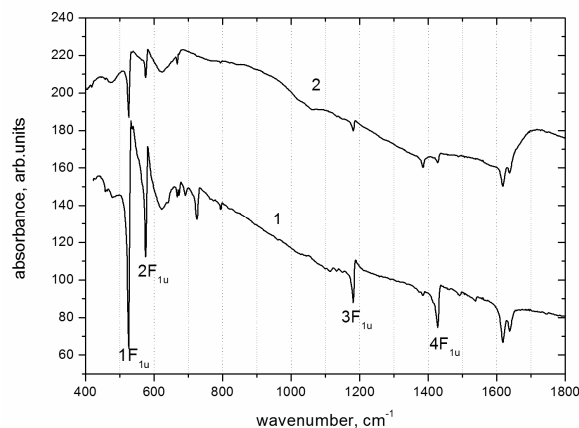


Fig. 2 IR-spectra of initial fullerene (1) and of the sample modified by $[\text{Ni}(\text{CoEtm}_3)_2](\text{NO}_3)_2$ complex pyrolyzed in Ar at 500°C (2). Four vibration bands of C_{60} are marked.

As follows from the spectra, the wavenumbers of four vibration modes of C_{60} , 1F_{1u} (526 cm^{-1}), 2F_{1u} (576 cm^{-1}), 3F_{1u} (1182 cm^{-1}), and 4F_{1u} (1428 cm^{-1}), are in good agreement with data reported in the literature [16]. The positions of these bands do not change after the modification, and no additional bands appear. On the contrary, the three bands at 692 cm^{-1} , 725 cm^{-1} and 795 cm^{-1} vanish. This may indicate the removal of oxygen-containing admixtures from the sample in the course of annealing the sample with grafted complex in inert atmosphere.

Thus, it seems that the modification of the fullerene does not affect the structure of the sample, and the catalytic effect consists in facilitating the charge transfer during the reduction process, as in the case of intercalation of Li into graphite [9,10].

As follows from the electrochemical experiments, the process of insertion of up to about 10 atoms of Li per molecule is irreversible, that is, it cannot be extracted upon application of a reverse anodic current. This fact is in agreement with the irreversible electrochemical behaviour of the lithium fulleride – mesoporous tantalum oxide reported in [17].

It is worthwhile noting that the structure of the Li fulleride with approximate composition $\text{Li}_{10}\text{C}_{60}$ is able to reversibly take up some additional amount of Li, about 4-5 atoms per formula. It can be repeatedly extracted from the sample in a reverse anode process (see the loop in curve 3, Fig. 1). It gives a reversible specific capacity of about $180 \text{ mAh}\cdot\text{g}^{-1}$. This capacity fades in the course of repeated cycling, as shown in Fig. 3. Thus, this result, being interesting from the scientific point of view, is so far not of practical importance for Li battery technology.

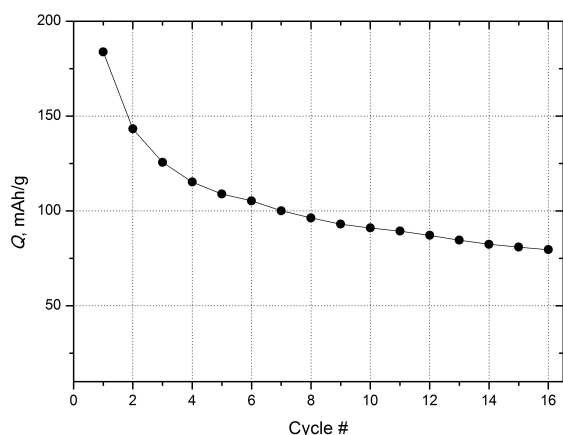


Fig. 3 Reversible capacity of lithium fulleride in the course of cycling.

Conclusions

A fulleride with high content of lithium (about $\text{Li}_{10}\text{C}_{60}$) could be obtained by electrochemical reduction of Li^+ ions on a fullerene-based electrode in the presence of the pyrolysis products of a $[\text{Ni}(\text{CoEtM}_3)_2](\text{NO}_3)_2$ complex as catalyst. The reaction proceeds irreversibly.

The compound is able to incorporate an additional amount of Li up to the composition $\text{Li}_{16}\text{C}_{60}$. This part of the reaction is electrochemically reversible – about 5-6 atoms of Li per formula can be extracted by means of anode current.

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