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**EFFECT OF THE ELECTROLYTE COMPOSITION ON THE
ELECTROCHEMICAL PROPERTIES OF BOTH NATURAL AND
SYNTHETIC GRAPHITE MATERIALS MODIFIED BY 2Co(+3)-Ni(+2)
COMPLEXES WITH AMINOALCOHOLS**

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The method of preparation and properties of the carbon materials modified by polynuclear complex compound 2Co-Ni with aminoalcohols have been used. As the graphite substrate used natural and synthetic origin. Were formed lithium ion electrochemical current sources with electrolytes based on lithium perchlorate and LiPF_6 . The combination of electrolyte and graphite certain origins helps to reduce cost in the manufacture of lithium ion elements along with improving their specific electrochemical characteristics.

Presently, synthetic or artificial graphites are the main materials for the negative electrodes of commercial Li-ion batteries. In order to improve the electrochemical properties of these materials (capacity, cycleability), various methods of their modification are currently under development. Among them, grafting of the heterometal trinuclear complexes of 2Me(+3)-Me(+2), in particular, 2Co(+3)-Ni(+2), with aminoalcohols, followed by pyrolysis in an inert atmosphere, proved to be very efficient [1,2].

The aim of this work was to find out how the composition of the aprotic organic electrolyte affects the properties of modified graphites of different origin (either synthetic or natural).

Research Methodology

Chemical purity grade cobalt $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and nickel $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ nitrates, potassium hydroxide KOH, monoaminoethanol (HEtm), diaminoethanol (H_2Detm) and triaminoethanol (H_3Tetm) and isopropanol were used for the synthesis of 2Co-Ni complexes. The syntheses were performed in two steps.

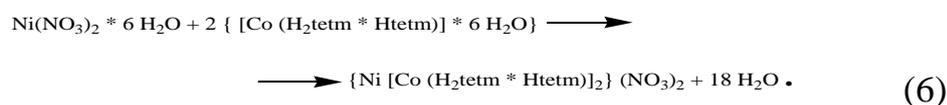
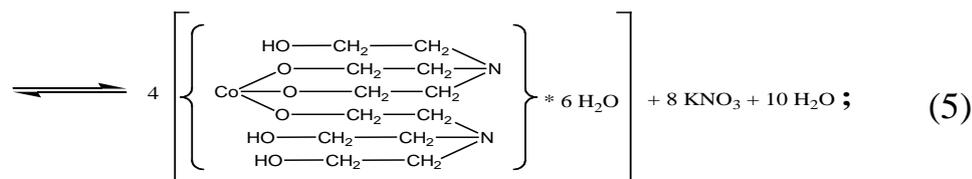
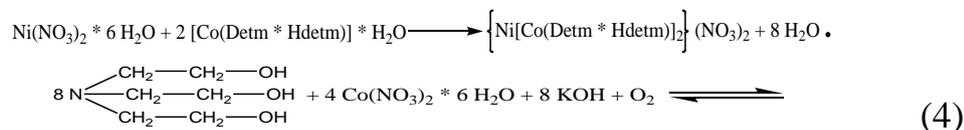
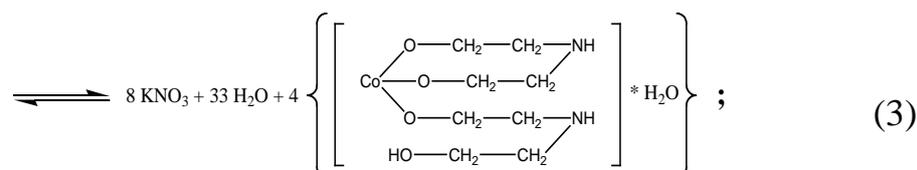
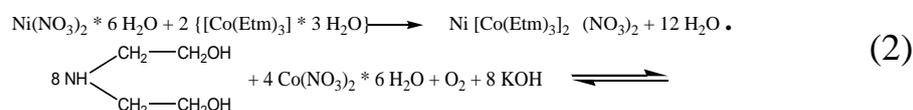
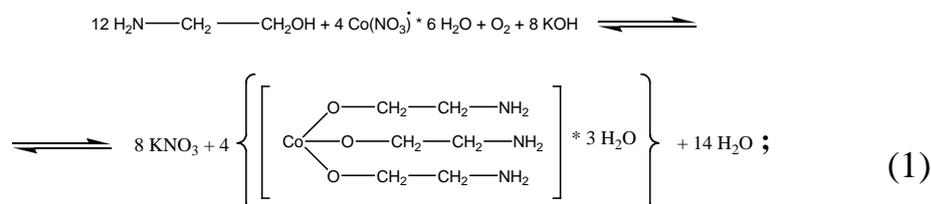
First, the inner complex Co(+3) compounds with each aminoalcohol were obtained. For this, the solutions of cobalt nitrate and potassium hydroxide in isopropanol were prepared. Further on, an overstoichiometric excess of the aminoalcohol was added to the cobalt nitrate solution (molar ratios $\text{Co}(\text{NO}_3)_2/\text{HEtm}$, $\text{Co}(\text{NO}_3)_2/\text{H}_2\text{Detm}$ and

Co(NO₃)₂/H₃Tetm were equal to 1/4, 1/4 and 1/2.2 accordingly), and after that, the potassium hydroxide solution was added. The mixture stayed at room temperature for 30 min, and formed potassium nitrate crystals were filtered out. The filtrate solution was aerated for 2-3 hours by means of a compressor. After that, the solution was aged for 3 days.

The chemical reactions (1), (3) and (5) correspond to the formation of the inner complex compounds with HEtm, H₂Detm and H₃Tetm accordingly.

The second step was the synthesis of trinuclear complex. It was performed as follows. The nickel nitrate was dissolved in isopropanol at 50-60°C, cooled down to the room temperature and added to the previously prepared solution of the inner complex compound at constant stirring. Thus obtained, the mixture was aged for 3 days.

The chemical reactions (2), (4) and (6) correspond to the formation of trinuclear complexes with HEtm, H₂Detm and H₃Tetm accordingly.



Two types of graphite materials were chosen for the investigation – synthetic LBG-73 (Superior Graphite Company, USA), and natural GP-1 (Ukraine). Their modification was performed by adsorption from isopropanol solution (0.05 mol of the complex per 1 g of graphite) with subsequent pyrolysis in high purity argon atmosphere. Adsorption time was 2 days. After that the material was filtered and dried at room temperature. The pyrolysis was carried out at 500⁰C, 550⁰C and 650⁰C for mono- di- and triaminoethanol complexes accordingly during 1 hour.

Investigation of the electrochemical properties of the modified graphite materials was performed in button 2016 size mock-up cells with Li counter-electrode. Two types of the electrolytes were tested – with lithium perchlorate LiClO₄ and lithium fluorophosphate LiPF₆. The salts were dissolved in equimolar mixture of ethylencarbonate (EC) and dimethylcarbonate (DMC). The assembled cells were tested in galvanostatic conditions using the 8-channel computer governed equipment.

Results and Discussions

The electrochemical behavior of natural and synthetic graphites in the perchlorate electrolyte is shown in Fig1 and Fig2.

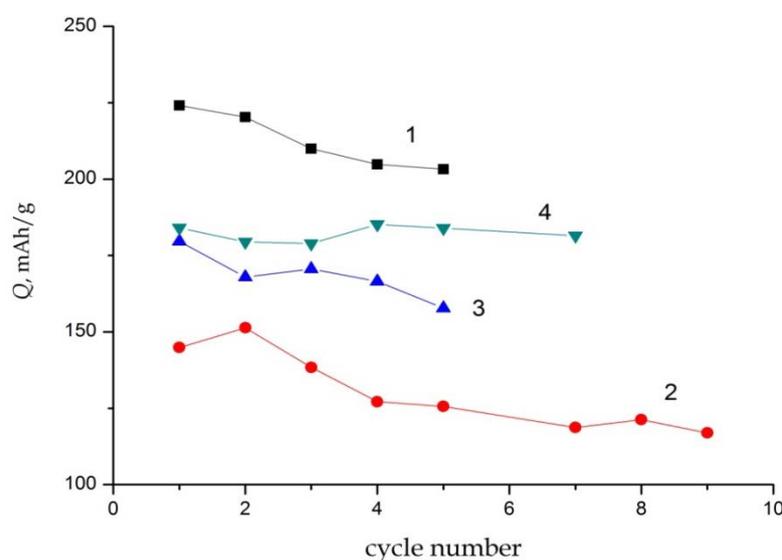


Figure 1. Specific discharge capacities vs. cycle number for natural graphite in perchlorate electrolyte:

1 – original, 2 – modified by monoaminoethanol, 3 – modified by diaminoethanol and 4 – modified by triaminoethanol pyrolysis products. Current load 10 mA/g

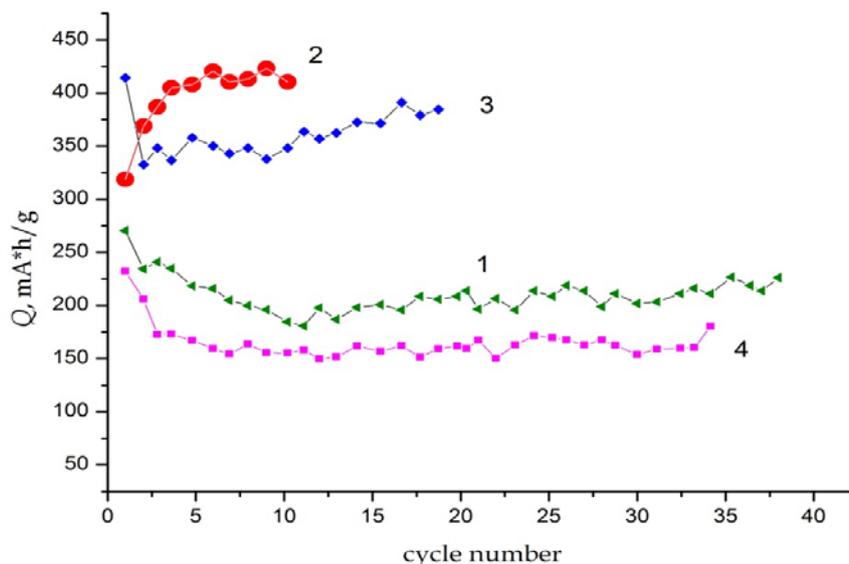


Figure 2. Specific discharge capacities vs. cycle number for synthetic graphite LBG-73 in perchlorate electrolyte: 1 – original, 2 – modified by monoaminoethanol, 3 – modified by diaminoethanol and 4 – modified by triaminoethanol pyrolysis products. Current load 10 mA/g

As follows from Fig1, no catalytic effect is observed for the modified samples of natural graphite in the perchlorate electrolyte. Meanwhile, the modification effect is quite pronounced for the artificial graphite.

The results of the modification is much better in case of hexafluorophosphate electrolyte, Fig3 and Fig4.

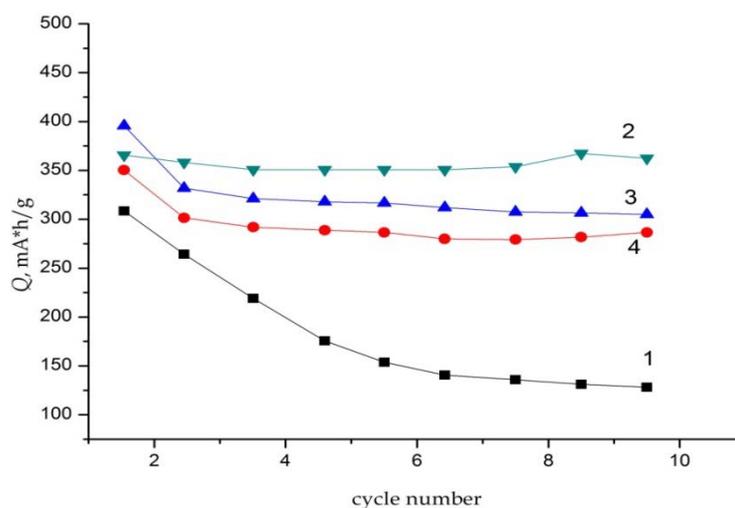


Figure 3. Specific discharge capacities vs. cycle number for natural graphite in hexafluorophosphate electrolyte: 1 – original, 2 – modified by monoaminoethanol, 3 – modified by diaminoethanol and 4 – modified by triaminoethanol pyrolysis products. Current load 10 mA/g

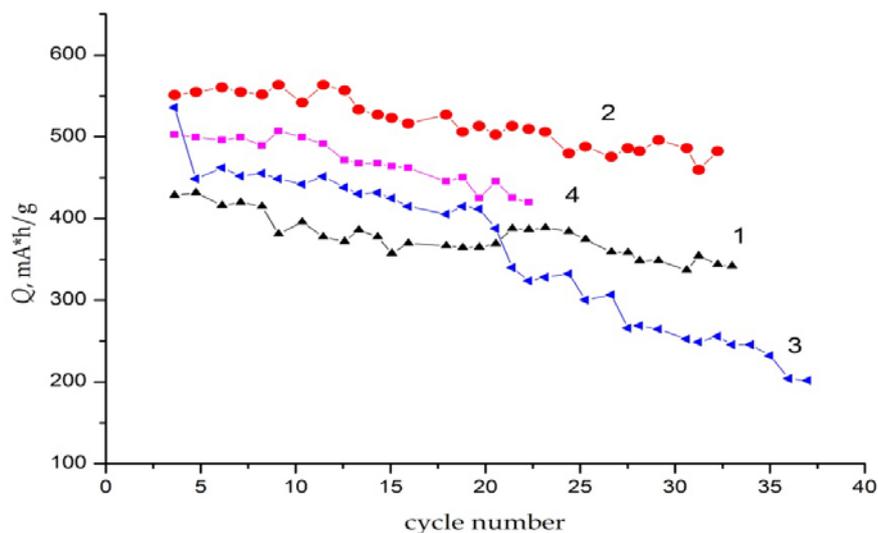


Figure 4. Specific discharge capacities vs. cycle number for synthetic graphite LBG-73 in hexafluorophosphate electrolyte: 1 – original, 2 – modified by monoaminoethanol, 3 – modified by diaminoethanol and 4 – modified by triaminoethanol pyrolysis products. Current load 10 mA/g

One can see that the electrochemical behavior of both natural and synthetic graphite can be significantly improved by means of the modification by monoaminoethanol pyrolysis products.

Conclusions

The effect of modification depends not only on the type of ligand and pyrolysis temperature, but on the type of the graphite and electrolyte as well. It was found that the catalytic effect is absent for the natural graphite in perchlorate electrolyte. Practically, modified natural graphite (which is cheaper) can be used in combination with hexafluorophosphate electrolyte. On the other hand, the cheaper and more environmentally friendly perchlorate electrolyte can be successfully used for the cells with the synthetic graphite.

References

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