Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 2, 503–506

A NEW METHOD OF COATING POWDERED SUPPORTS WITH CONDUCTIVE CARBON FILMS

M. Molenda[1], *R. Dziembaj*[1,2*], *Z. Piwowarska*[1] *and M. Drozdek*[1]

[1]Faculty of Chemistry, Jagiellonian University, Ingardena 3 Str., 30-060 Cracow, Poland
[2]Regional Laboratory of Physicochemical Analyses and Structural Research, Ingardena 3 Str., 30-060 Cracow, Poland

A series of conductive composite materials were obtained by polymerization of acrylonitrile in water suspensions of Al_2O_3 powder followed by further carbonization of the polymeric films covering the Al_2O_3 grains. The electrical conductivity and activation energy of the composites were measured in relation to the parameters used in preparation of the samples. This highly effective procedure can be used to improve electrical conductivity of the cathodes in lithium ion batteries.

Keywords: *carbon coating, carbon conductive layers, DSC, electrical conductivity, lithium ion batteries, TG*

Introduction

The high performance of lithium ion batteries can be achieved only with cathode materials showing high enough ionic and electronic conductivities. Currently, the standard composite cathodes are prepared by mixing together: 85–90% of the active cathode material ($LiCoO_2$, $LiNi_{0.5}Co_{0.5}O_2$), 10–15% of the carbon additives (graphite, carbon black) and binder (PVdF – polyvinylidene fluoride) [1, 2]. However, such a method of preparation may cause lowering of the reversible cell capacity due to limitation in the charge transport in the composite cathode. In consequence, the active material is not fully exploited [3, 4]. There are reports that the cathode materials coated by carbon [5–9], polymers [10, 11] as well as by another cathode material (coating of $LiMn_2O_4$ by $LiCoO_2$ [12]) improves significantly the electrochemical properties of such composite cathodes. However, the proposed methods of the composite preparation are difficult to apply on industrial scale.

The present paper proposes a novel preparation of the cathode composites for Li-ion batteries. It is obvious that coating of the surface of active materials by conductive carbon layers (CCL) should provide sufficient electron-conductive network (Fig. 1). Moreover, the thin CCL are usually not continuous layer providing good pathways for mobile lithium ions. We have prepared the CCL by pyrolysis of polymer precursors (acrylonitrile – AN) deposed directly on the surface of supporting material. To avoid any side reaction with polymer precursor as well as with carbon deposit during pyrolysis process an inert support (α-Al_2O_3, POCh) was used. The detailed conditions for pyrolysis the samples were optimized based on results of introductory TG and DSC measurements, like it was used in [13]. The electrical properties of the C/Al_2O_3 composites were determined by ac 4-probe method.

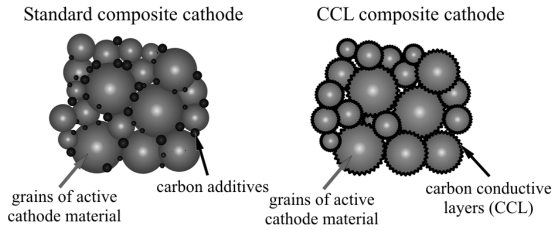

Fig. 1 Comparison of the standard composite cathode *vs.* model of the CCL composite cathode for Li-ion batteries

Experimental

The polymerization of acrylonitrile (AN) was done by radical, precipitation polymerization in aqueous solution. The reaction was performed in a glass reactor under constant flow of argon. Freshly distilled AN was dissolved at 25°C in de-ionized water flushed previously with Ar for 30 min. The initiator, 2,2'-azobis(isobutyramidine hydrochloride) (AIBA, Aldrich), was subsequently added and the reaction mixture was heated up to 60°C for 3 h. The obtained polyacrylonitrile (PAN) was filtered and washed with distilled water and then dried under vacuum at 50°C. The polymer was pyrolysed under flow of argon (10 $dm^3 h^{-1}$) within temperature range of 400–800°C for 12 h.

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* Author for correspondence: dziembaj@chemia.uj.edu.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 Compositions of the initial reaction mixture and resulting composites C/Al_2O_3

Sample	AN:Al_2O_3	I:N*	C content in C/Al_2O_3 composites/%	
			pyrolysis at 400°C/12 h	pyrolysis at 700°C/12 h
1	0.8:1	0.002	–	4.5
2	0.8:1	0.004	5.1	4.9
3	1.2:1	0.004	10.3	8.5
4	1.6:1	0.004	20.6	17.9
5	2:1	0.004	37.2	31.5

*Initiator (AIBA) to monomer (AN) ratio

The composites PAN-Al_2O_3 were obtained by radical polymerization of AN in water suspension of Al_2O_3 with analogue procedure to described above. The carbon composites (C/Al_2O_3) were prepared by controlled pyrolysis of the prepared PAN-Al_2O_3 precursor within conditions determined from PAN pyrolysis. The amount of carbon in the obtained C/Al_2O_3 composites was determined by temperature programmed oxidation (TPO) performed in TG apparatus coupled with mass spectrometer (QMS). The compositions of the initial reaction mixture and resulting composites composition are collected in Table 1.

The thermal gravimetry analysis coupled with mass spectrometry analysis (MS-TG/DTG/SDTA) experiments were performed in Mettler-Toledo 851^e apparatus in 150 μL corundum crucibles under flow of argon or air (80 mL min^{-1}), within temperature range 25–1000°C with heating rate of 5°C min^{-1}. The simultaneous evolved gas analysis (EGA) was performed during the experiments by joined on-line quadruple mass spectrometer (QMS) (Thermostar-Balzers).

Differential scanning calorimetry (DSC) experiments were performed in Mettler-Toledo 821^e calorimeter equipped with intracooler Haake in 40 μL aluminium crucibles under constant flow of argon (80 mL min^{-1}) within temperature range 25–600°C with the same heating rate of 5°C min^{-1} as TG measurements.

Electrical conductivity was measured using ac 4-probe method within temperature range of –40–55°C. Measured powder samples were placed between parallel gold disc electrodes and pressed by a screw-press till the measured resistance does not changed.

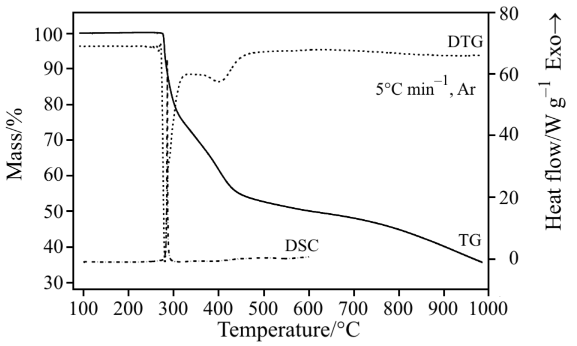

Fig. 2 TG/DTG/DSC curves of polyacrylonitrile (PAN) pyrolysis

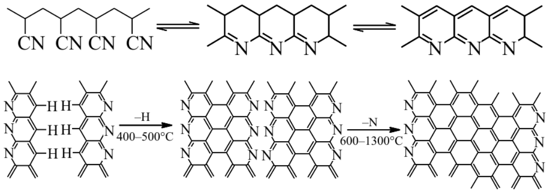

Fig. 3 Mechanism of the PAN pyrolysis and graphitization

Results and discussion

The results of thermal analysis (TG/DTG/DSC) during pyrolysis of polyacrylonitrile (PAN) is presented in the Fig. 2. The pyrolysis starts above 270°C and may be divided into three stages. The first one (270–350°C) is related to 25% mass loss and is accompanied with a strong exothermic effect. It must be related to cyclization of PAN chains and formation of aromatic structure of the polymer (Fig. 3). The second mass loss (350–450°C) should be ascribed to carbonization and dehydrogenation of the material and formation of the condensed structure. The last stage of the PAN pyrolysis (above 450°C) is related to loss of nitrogen and graphitization of the carbonaceous material. The local structure of the obtained carbons was defined by Raman spectroscopy measurements in another paper [14] supporting the proposed mechanism of PAN pyrolysis.

Electrical properties of the PAN pyrolysed carbons obtained within 400–800°C under argon atmosphere are presented in Fig. 4. The electrical conductivity of the sample pyrolysed at 400°C is in the range of 10^{-6} S cm^{-1} and increases with increasing of the pyrolysis temperature. Above 600°C, the electrical conductivity of the carbon material reaches 10^{-2} S cm^{-1} and this value is sufficient for the Li-ion purposes, though higher temperatures provide even higher electrical conductivity. Activation energy

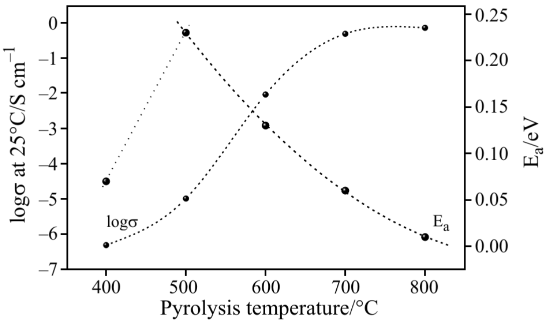

Fig. 4 Electrical properties of the carbon derived from PAN pyrolysis

of the electrical conductivity (Fig. 4) decreases with increase of pyrolysis temperature (500–800°C), presumably in results of progressive graphitization of the carbon structure.

The sample decomposed at 400°C shows the lowest activation energy and electrical conductivity. This suggests that the charge transport is realized only by small number of surface graphite domains. We have found that the optimal temperature of PAN pyrolysis is above 600°C, and it needs about 12 h baking under flow of argon.

The chemical composition of the carbonized samples (C/Al_2O_3) was determined by TPO. The carbon deposits were oxidatively gasified in the thermobalance within temperature range of 25–1000°C with heating rate of 5°C min^{-1} in air (Fig. 5). The oxidation of carbonaceous deposits occurs between 410 to 630°C accompanying with an exothermic effect proportional to carbon content. The obtained results for the composites are collected in Table 1.

Electrical properties of the C/Al_2O_3 composites prepared at 700°C under argon atmosphere are presented in Fig. 6. Electrical conductivity of the composites increases continuously with increase of the carbon content, however two regions of the changes may be distinguished. In the first one, up to 10–12 mass% C, the electrical conductivity increases very fast (3 orders of magnitude) due to formation of the percolation paths. This is accompanied by increase of the activation energy of the electrical conductivity (from 0.04 to 0.09 eV), what suggests that the charge transport mechanism changes from the surface conductivity on the graphite nanodomains to bulk mechanism through the conductive carbon layer. It must be noticed that electronic charge transport is realized only by CCL, because the host material (α-Al_2O_3) is an electrical insulator. Further increase of the carbon content (above 15 mass% C) increases the electrical conductivity only within one order of magnitude, and moreover, the activation energy of electrical conductivity does not change being equal to 0.09 eV. Such a value is slightly higher than that for the carbon films obtained at the same conditions (700°C, 12 h, Ar), which is equal to 0.06 eV. This may be explained by interaction between π electrons of graphite like carbon in the CCL and the support (α-Al_2O_3).

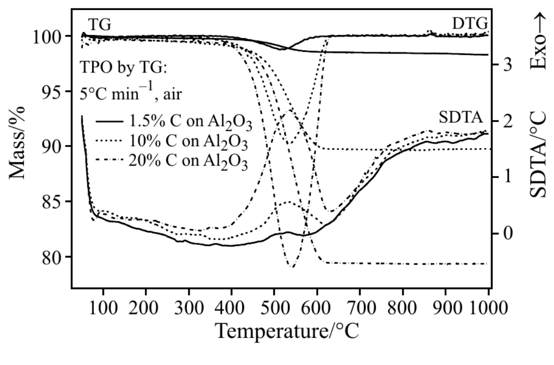

Fig. 5 Determination of carbon content in the composites by TPO

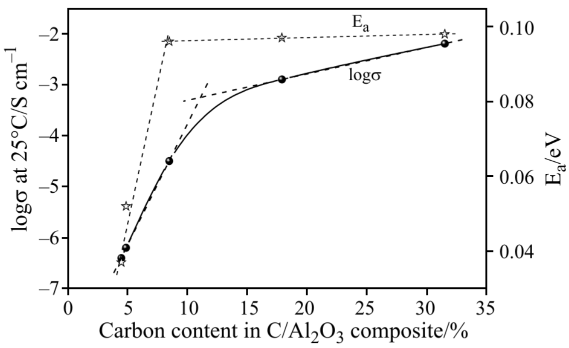

Fig. 6 Electrical properties of the C/Al_2O_3 composites prepared at 700°C/12 h

Conclusions

The precipitation polymerization of AN in water suspension of Al_2O_3 powder results in formation of PAN layer covering the surface of the oxide grains. This layer is transformed into carbon conductive layer (CCL) by controlled treatment forming the C/Al_2O_3 composite showing electrical conductivity better than 10^{-3} S cm^{-1} with E_a=0.09 eV. The new method of preparation can be adopted to obtain carbon composites for cathodes in Li-ion batteries with improved electrical conductivity in relation to the present available ones. A trial has been performed in a separate paper [14].

Acknowledgements

This work has been financially supported by the Polish Ministry of Science and Higher Education under grant no. 3 T08D 010 28. One of the authors (M. M.) would like to acknowledge the Foundation for Polish Science for the support in the form of The Annual Stipend for Young Scientists.

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DOI: 10.1007/s10973-006-8226-6