

Short communication

An attempt to improve electrical conductivity of the pyrolysed carbon-LiMn₂O_{4-y}S_y (0 ≤ y ≤ 0.5) composites

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Available online 27 June 2007

Abstract

An attempt to obtain conductive carbon layer (CCL) on the LiMn₂O₄ and LiMn₂O_{4-y}S_y spinels, using the radical precipitation polymerization of acrylonitrile (AN) and styrene–acrylonitrile (SAN) in water suspension of the spinels followed, by pyrolysis of the composed precursors was made. In the case of PAN–spinel precursors the CCL on spinel particles was effectively formed. Phase transitions, as well as thermal and electrical properties of the carbon-sulphided spinel composites were characterized. An attempt with SAN copolymer failed due to the reaction between SAN and the spinels during pyrolysis, even in the argon stream.

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Keywords: Li-ion cathodes; Sulphided Li–Mn spinels; Carbon coating; Precipitation polymerization; Electrical conductivity; Phase transitions

1. Introduction

The materials currently used in high power Li-ion batteries, like LiCoO₂ and LiNi_{0.5}Co_{0.5}O₂, are toxic and expensive [1,2]. LiMn₂O₄ spinel, which is discussed as a replacement material, is distinctly cheaper and less toxic. Hence, this spinel and related systems [1–4] were considered as promising materials for electric vehicles (EV) or hybrid electric vehicles (HEV) [5] in numerous papers. Commercialization of the cathode materials based on LiMn₂O₄ system has been delayed mainly because of their structural instability. Furthermore, surface of these materials reveals insufficient resistance against electrolyte and needs to be improved [6,7].

The stoichiometric LiMn₂O₄ shows a reversible phase transition from cubic (*Fd3m*) to orthorhombic (*Fddd*) structure near room temperature [8], resulting in the fading of the electric capacity of the cathode materials in consecutive cell cycling. Such phase transition is related to the Jahn–Teller distortion of high-spin Mn³⁺ ions located in high symmetry (*O_h⁷*) sites [9,10]

and specific charge ordering in manganese sublattice [11–13]. Stabilization of the high temperature structure (cubic phase) may be performed by partial substitution of Mn³⁺ ions by 3d metal ions (Cr, Fe, Ni, Co) [14,15], Al³⁺ [16] ions or Li⁺ ions excess [17–19].

Both modifications cause serious decrease of Mn³⁺/Mn⁴⁺ ratio due to the necessary charge compensation in crystal lattice. In consequence, remarkable decrease in 4 V capacity is observed. In previous papers [20–22] we proposed another modification of the spinels, applying partial izoelectronic substitution of oxygen atoms with sulphur in anionic sublattice. Such a modification seemed sufficient to suppress the Jahn–Teller effect as well the RT phase transition.

Surface side reactions of the spinel cathodes with electrolyte provide formation of SEI layer [6,7]. These reactions arise from instability of Mn³⁺ surface ions due to their disproportionation into soluble Mn²⁺ ions and insoluble Mn⁴⁺ ones. The Mn²⁺ ions dissolved in electrolyte catalyze its decomposition. Enrichment of the cathode surface in Mn⁴⁺ ions increases electrical resistance. Both effects result in decrease of the current density in the Li-ion cell. Covering spinel cathodes by an inert but conductive material should protect the surface against destruction by the reactive electrolytes.

There are reports that surface coating of cathode material by carbon [23], polypyrrole (PPy) [24] and another cathode material

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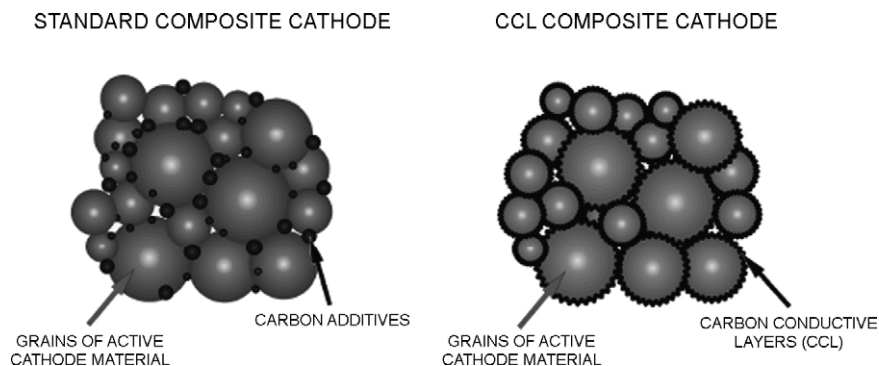


Fig. 1. The models of composite cathodes.

(coating of LiMn_2O_4 by LiCoO_2) [25] distinctly improves electrochemical properties of such composite cathodes. However, the proposed methods of the composite preparation are difficult to scale-up on industrial scale. The high performance of Li-ion batteries can be achieved only with cathode materials with sufficiently high ionic and electronic conductivity. Currently, standard composite cathodes are prepared by mixing together: 85–90% of the active cathode material, 10–15% of the carbon additives (graphite, carbon black) and binder (PVDF). However, such a method of preparation may cause lowering of the reversible cell capacity due to the limitation of charge transport in the composite cathode. In consequence, the active material is not fully exploited [26,27]. In the recent work we have proposed a novel method of preparation of the carbon composites derived from polymeric precursors [28]. 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 providing good pathways for mobile lithium ions. These promising results have been achieved by pyrolysis of polymeric precursors (polyacrylonitrile) deposited directly on the surface of a model support Al_2O_3 . The carbon precursor layer was obtained by in situ precipitation polymerization in water suspension of the support. This method is different from the usually used one based on mixing carbon precursors with active cathode materials [22,29,30].

The present work is an attempt to prepare carbon–spinel composites with the use of direct precipitation polymerization, forming precursors for the CCL–spinel composites. Applicability of this method will be revealed and the optimal conditions will be determined. The electrical properties of the obtained materials will be characterized.

2. Experimental

A set of sulphur modified lithium–manganese spinels $\text{LiMn}_2\text{O}_{4-y}\text{S}_y$ ($0.0 \leq y \leq 0.5$) were obtained by the sol–gel method described elsewhere [20,21]. The samples were calcined within temperature range 300–800 °C in air for 6–24 h and quenched, in order to obtain materials with different properties and defect structure and, in consequence, to find the optimal conditions of their preparation.

The crystal structure of the sulphided spinels obtained at various conditions (composition, temperature, time) were char-

acterized by X-ray powder diffraction technique on *PW3710 Philips X'Pert* apparatus using $\text{Cu K}\alpha_1$ ($\lambda = 0.154178$ nm) radiation with a graphite monochromator [21]. The local structure of the obtained materials was determined by Raman spectroscopy [22].

The composites were obtained by radical precipitation polymerization of acrylonitrile (AN) or AN and styrene (S) in water suspension of the spinels with the following procedure. The polymerization was performed in a glass reactor under constant flow of argon. Freshly distilled monomers (AN or AN and S) were dissolved at 25 °C in de-ionized water, flushed previously with Ar for 30 min. The initiator, AIBA (Aldrich) was subsequently added and the reaction mixture was heated up to 60 °C for 3 h. The obtained spinel composites with polyacrylonitrile (PAN) or co-poly-styreneacrylonitrile (SAN) were filtered and washed with distilled water and then dried under vacuum at 50 °C. The optimal conditions of PAN pyrolysis were determined in the previous paper [28]. The composite precursors were pyrolysed under flow of argon ($10 \text{ dm}^3 \text{ h}^{-1}$) within temperature range of 400–900 °C for 12 h. The amount of carbon in the obtained C–spinel composites was determined by thermo-programmed oxidation (TPO) performed in TGA apparatus coupled with mass spectrometer (QMS).

The thermal gravimetric analysis (TGA) coupled with mass spectrometry analysis (MS-TGA/DTG/SDTA) was performed in *Mettler-Toledo 851^e* apparatus in 150 μl platinum crucibles under air flow (80 ml min^{-1}), within temperature range 30–1000 °C, with heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. The simultaneous evolved gas analysis (EGA) was performed during the experiments by joined on-line quadruple mass spectrometer (QMS) (*Thermostar-Balzars*).

The differential scanning calorimetry (DSC) experiments were performed in *Mettler-Toledo 821^e* calorimeter equipped with intracooler *Haake* in 40 μl aluminum crucibles under constant flow of argon (80 ml min^{-1}). The structural stability measurements were done within temperature range –40 to +60 °C with the cooling and heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The measurements of polymers pyrolysis were performed within temperature range +25 to +600 °C with heating rate of $5 \text{ }^\circ\text{C min}^{-1}$.

Raman measurement was performed on thin pellets containing 10 mg of the sample and 200 mg of KBr. The spectra were recorded at room temperature using a triple grating spec-

trometer (Jobin Yvon, T 64000). A liquid nitrogen cooled CCD detector (Jobin Yvon, Model CCD3000) was used in these measurements. The spectral resolution of 2 cm^{-1} was set. An excitation wavelength at 514.5 nm was provided by an Ar-ion laser (Spectra-Physics, Model 2025). The laser power at the sample position was about 20 mW (32 W cm^{-2}). Such a low power of laser radiation was required to prevent any decomposition of the samples. Raman scattered light was collected with a 135° geometry, and 5000 scans were accumulated to ensure acceptable signal-to-noise ratio.

Electrical conductivity was measured using *ac* (33 Hz) 4-probe method within temperature range of -40°C to $+55^\circ\text{C}$ on pellets pressed by hydraulic press (5 tonnes) or on powder samples placed between parallel gold disc electrodes and pressed by a screw-press till the measured resistance did not change. To improve the electrical contact between pellets and electrodes a silver paste with acrylic resin was used.

3. Results and discussion

3.1. Properties of the $\text{LiMn}_2\text{O}_{4-y}\text{S}_y$ spinel

Structural stability of the obtained sulphided spinels is presented in Fig. 2a. The observed heat effects during heating and cooling cycles are related to the first order phase transition (cubic \leftrightarrow orthorhombic) in the spinel structure. The sulphur substitution into oxygen sublattice provides stabilization of

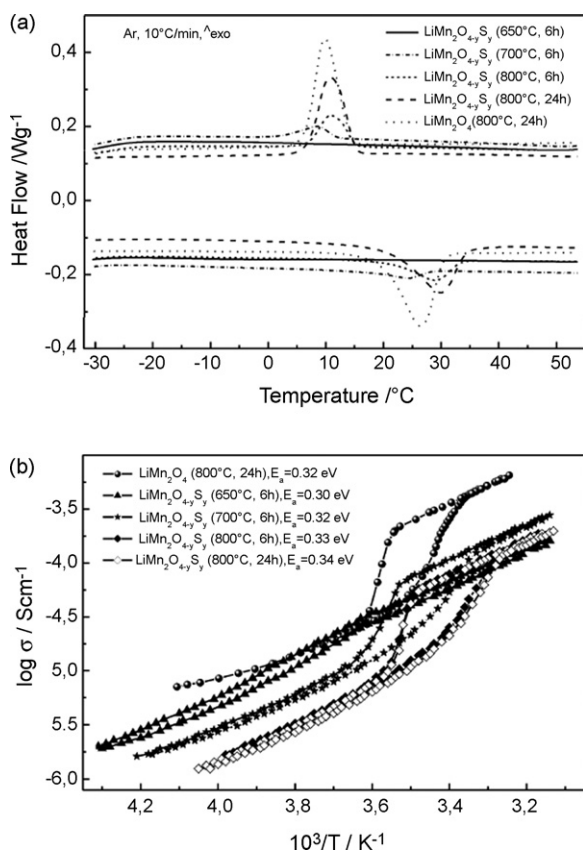


Fig. 2. The effect of temperature and time of calcination on DSC structural stability (a) and on electrical properties (b).

the regular spinel structure in comparison to stoichiometric LiMn_2O_4 spinel. However, the smaller heat effects related to the phase change are still present. Decrease of the calcination time from 24 to 6 h as well as lowering of the calcination temperature provides improvement of electrical and structural properties. The sulphur substituted spinel $\text{LiMn}_2\text{O}_{4-y}\text{S}_y$ obtained by calcination at 650°C for 6 h was stable and showed no heat effects on DSC curves (Fig. 2a). The results of measurements of the electrical conductivity are presented in Fig. 2b. The obtained results are in good accordance with DSC results. However, the sulphur-stabilized spinels show unfortunately lower electrical conductivity in relation to stoichiometric LiMn_2O_4 spinel. An improvement can be achieved also by lowering of the calcination time to 6 h and the temperature to 650°C . Such material provides quite acceptable electrical conductivity. Moreover, this material reveals the lowest activation energy of 0.30 eV , even in relation to LiMn_2O_4 spinel ($E_a = 0.32\text{ eV}$). We hope that new synthesized C- $\text{LiMn}_2\text{O}_{4-y}\text{S}_y$ composites will help to achieve materials of fully satisfactory electrical conductivity.

Thermal stability of Li–Mn–O and Li–Mn–O–S spinels in air atmosphere was determined in previous papers [10,17,19,21]. In the case of carbon–spinel composites formation, during pyrolysis of the polymer carbon precursor, has to be performed in an inert atmosphere (Ar, 99.999%). In such an atmosphere we have observed thermal stability of the spinels up to 600°C .

3.2. Properties of the conductive carbon layers (CCL)

The results of thermal analysis (TG/DTG/DSC) during pyrolysis of polyacrylonitrile (PAN) are presented in Fig. 3. The pyrolysis starts above 270°C and may be divided into three stages. The first ($270\text{--}350^\circ\text{C}$) one is related to 25% mass loss and is accompanied by a strong exothermic effect. It is related to cyclization of PAN chains and formation of aromatic structure of the polymer [28]. The second stage of mass loss ($350\text{--}450^\circ\text{C}$) is due to carbonization and dehydrogenation of the material and formation of the condensed structure [28]. The last stage of the PAN pyrolysis (above 450°C) is related to loss of nitrogen and to formation of the carbonaceous material [28]. The local structure of the obtained carbon materials was defined by Raman spectroscopy (Fig. 4). Two vibration bands observed at

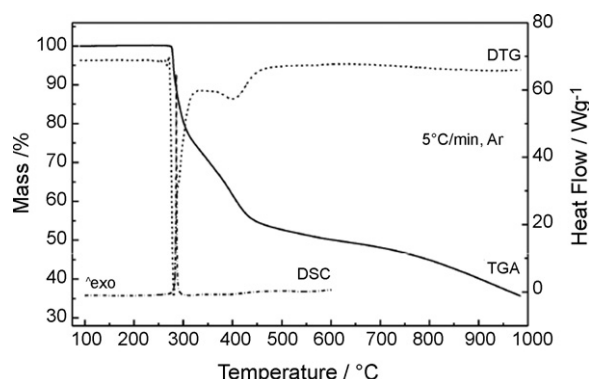


Fig. 3. The TG/DTG/DSC results of PAN pyrolysis.

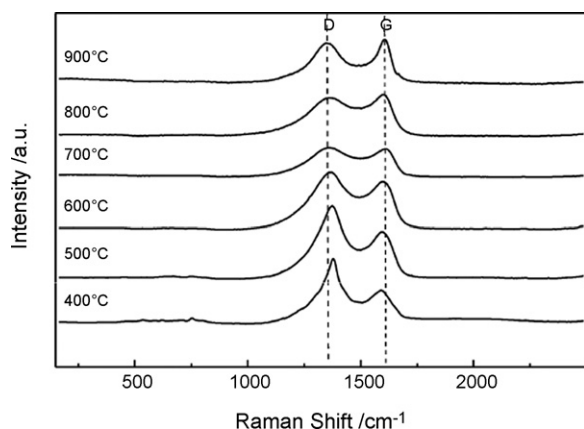


Fig. 4. Raman spectra of the carbons derived from PAN pyrolysis at different temperatures.

circa 1360 and 1600 cm^{-1} are related to D (disordered) and G (graphene) bands [29], respectively. During increase of pyrolysis temperature, the intensity of graphite G band increases while the intensity of D band decreases, confirming progressive graphitization of the carbonaceous materials derived from PAN precursor.

Electrical properties of the PAN pyrolysed carbons obtained within 400 – $800\text{ }^{\circ}\text{C}$ under argon atmosphere are presented in Fig. 5. The electrical conductivity of the sample pyrolysed at $400\text{ }^{\circ}\text{C}$ is in the range of 10^{-6} S cm^{-1} and increases with the increase of the pyrolysis temperature. The electrical conductivity of the carbon material pyrolysed at $600\text{ }^{\circ}\text{C}$ reaches the value 10^{-2} S cm^{-1} , which is sufficient for the *Li-ion* batteries purposes, though higher temperatures provide even higher electrical conductivity. Activation energy of the electrical conductivity (Fig. 5) decreases with increase of the pyrolysis temperature (500 – $800\text{ }^{\circ}\text{C}$) in result of progressive graphitization of the carbon structure.

The sample decomposed at $400\text{ }^{\circ}\text{C}$ shows the lowest activation energy and electrical conductivity. This suggests that the charge transport is realized only by a small number of surface graphite domains. In conclusion, the lowest possible temperature of pyrolysis is $600\text{ }^{\circ}\text{C}$ for at least 12 h in pure argon flow. Prolonged calcination at higher temperatures improves the electrical properties.

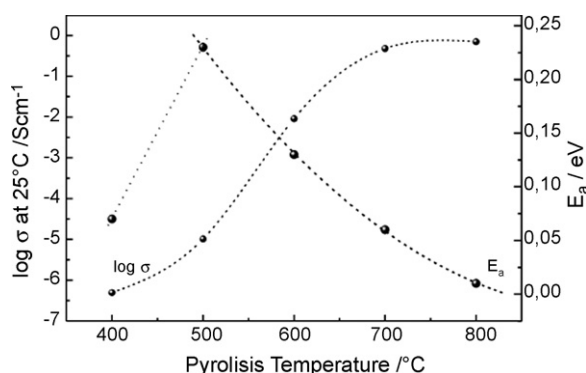


Fig. 5. Electrical properties of the carbons derived from PAN pyrolysis for 12 h at different temperatures in argon flow.

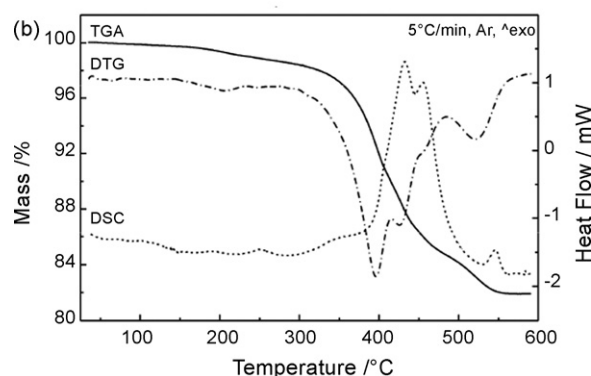
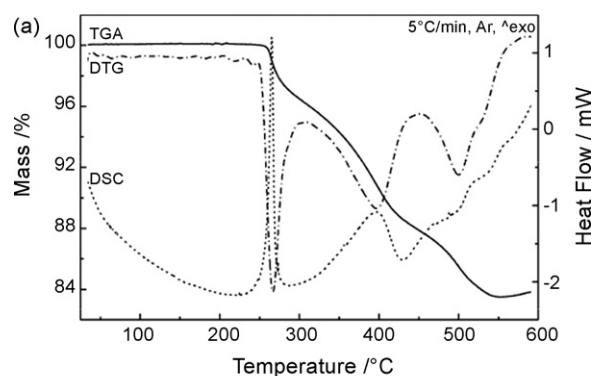


Fig. 6. Thermal analysis of pyrolysis of the composite precursors: PAN–spinel (a) and SAN–spinel (b).

3.3. Properties of CCL–spinel composites

The CCL composites were prepared by radical precipitation polymerization in water suspension of the spinel. Two kinds of polymers were used as carbon precursor: polyacrylonitrile (PAN) and random copolymer of styrene and acrylonitrile (SAN). Advance in pyrolysis has been studied using methods of thermal analysis (TGA/DTG/DSC). The results are presented in Fig. 6.

Decomposition of PAN–spinel precursors (Fig. 6a) starts above $270\text{ }^{\circ}\text{C}$ and is accompanied by a strong exothermic effect ascribed to cyclization of polymer chains, similarly as in the case of pyrolysis of PAN (Fig. 3). At circa $400\text{ }^{\circ}\text{C}$ an additional exothermic effect appears, probably due to side surface reactions between carbon deposit and spinel. Oxidation of the carbon deposit by spinel is observed above $450\text{ }^{\circ}\text{C}$, causing destruction of the composite. Hence, the optimal temperature for pyrolysis of PAN–spinel composite precursor should be $400\text{ }^{\circ}\text{C}$ under argon atmosphere for 12 h.

The electrical properties of CCL composite are related to the presence of condensed aromatic structure in the carbon deposit. Starting from this assumption we have tried to apply monomer with aromatic rings, namely styrene, as a copolymer with acrylonitrile (SAN). The thermal decomposition of SAN–spinel composite precursor is presented in Fig. 6b. The decomposition starts above $350\text{ }^{\circ}\text{C}$ and is accompanied by a strong exothermic effect with two overlapped steps. The process stops at about $550\text{ }^{\circ}\text{C}$, in contrast to PAN–spinel composite (Fig. 6a).

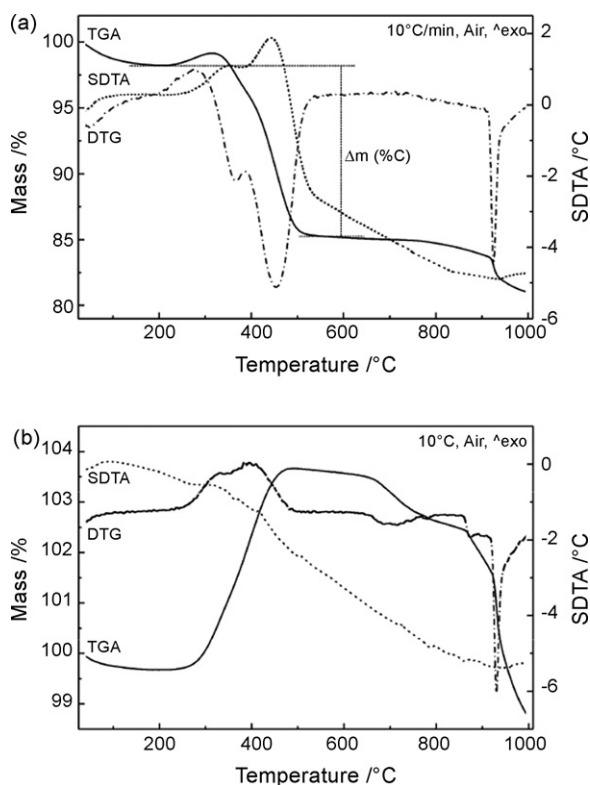


Fig. 7. Determination of carbon content in the composites obtained from: PAN-spinel (a) and SAN-spinel (b) composite precursors.

The carbon content in the obtained composites was determined by temperature programmed oxidation (TPO) in the thermo-balance within temperature range of 25–1000 °C with heating rate of 5 °C min⁻¹ in the dry air (Fig. 7), as it was done in previous paper on model substrate (Al₂O₃) [28].

For the CCL composite obtained from the PAN-spinel precursor the oxidation of carbonaceous material occurs between 380 to 530 °C and is accompanied with heat evolution (Fig. 7a). This is a two-step process and is clearly recognized on DTG curve. Probably, two kinds of carbon deposits are present in the composite. The temperature range of oxidation of carbon deposits in the C-spinel composite is much narrower (150 °C) than that for the model C-Al₂O₃ composite (220 °C). For the last, the carbon deposit oxidation started at the higher temperature (410 °C) [28]. This difference may be explained by a catalytic effect of manganese ions.

TPO tests on composites obtained from the SAN-spinel precursors did not prove the presence of the deposited carbon (Fig. 7b). Most probably, it was caused by the direct redox reaction between SAN copolymer and spinel during the carbonization procedure. As a result of that, spinel oxidized SAN precursor to carbon oxides. In previous papers [10,13,20] we observed reductive decomposition of the LiMn₂O₄ spinel in argon and even in air atmosphere with the formation of oxygen, Mn₃O₄ and LiMnO₂. It took place at temperatures higher than 600 and 920 °C, respectively, for argon and air atmosphere.

In the case of PAN-spinel precursors, an effective covering of the spinel grains by CCL was achieved. However, the electrical conductivity of the composite was lower than the expected one

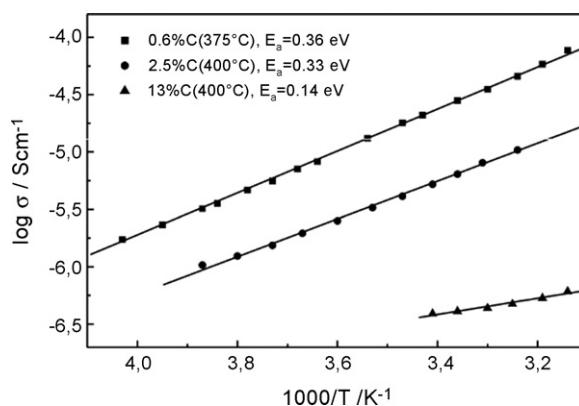


Fig. 8. Electrical conductivity of C-spinel CCL composites derived from PAN-spinel precursors.

(Fig. 8). It is possible that the temperature was too low to form the highly conductive carbon layer. Application of significantly higher carbonization temperature must be excluded because of the above mentioned redox reaction between spinel and PAN polymer. Further research for a less reductive polymers and/or undergoing of the partial graphitization at much lower temperature is necessary to obtain a composite material with improved electrical properties.

It should be reminded that highly conductive layer was achieved for PAN/Al₂O₃ composite obtained by carbonization at 700 °C. For example, 15 wt% of carbon in the C-Al₂O₃ composite revealed the electrical conductivity in the range of 10⁻² S cm⁻¹ [28]. The values of electrical conductivity of the C-spinel composites obtained from PAN-sulphided spinel precursors are similar to the values measured for materials obtained by carbonization of PAN alone at 400 °C (Fig. 5). It supports the assumption of continuous CCL being formed, which should strongly improve the chemical stability of the spinel surface against the electrolyte in batteries, though additional studies are necessary.

4. Conclusions

The radical precipitation polymerization of acrylonitrile in water suspension of fine particles alumina, followed by carbonization of the precursors resulted in formation of highly conductive carbon layers on the Al₂O₃. This method can be adopted to obtain the precursors for the conductive, carbon coated, LiMn₂O₄ and LiMn₂O_{4-y}S_y spinel composites. However, the temperature of the precursor carbonization has to be limited because of the redox reaction of spinels with polymeric coating. This coating shows no effect on the suppression of phase transition in room temperature of the spinels resulting from sulphur substitution of oxygen anions. It was proved by DSC, Raman spectra and electrical conductivity measurements. Further search for polymer precursors, able to form of highly conductive carbon layers at lower temperatures than 400 °C, is necessary. However, styrene-containing copolymers must be excluded, according to observed early reductive decomposition of the spinel lattice in the course of carbonization.

Acknowledgments

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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