

Short communication

Studies on self-assembly phenomena of hydrophilization of microporous polypropylene membrane by acetone aldol condensation products: New separator for high-power alkaline batteries

Aleksander Ciszewski^{a,*}, Bożena Rydzyńska^b

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

^b *Central Laboratory of Batteries and Cells, ul. Forteczna 12, 61-362 Poznan, Poland*

Received 5 October 2006; received in revised form 10 January 2007; accepted 17 January 2007

Available online 25 January 2007

Abstract

Commercial hydrophobic polypropylene (PP) membranes were modified by a novel chemical method. This procedure consists of two steps. In the first step, the virgin hydrophobic PP membrane is saturated with acetone; in the second step, the filled membrane is dipped in aqueous KOH solution ($d = 1.28 \text{ g cm}^{-3}$), i.e. in the electrolyte typical for the nickel–cadmium cell. This two-step procedure starts the aldol condensation process of acetone and its products accumulated and adsorbed onto walls of micropores make the membrane hydrophilic. The presented method provided the hydrophilic PP membrane, persistent and soaked with KOH solution with electrolytic resistance of 23–29 $\text{m}\Omega \text{ cm}^2$. This result was compared with the data obtained with commercial hydrophilic membranes: Celgard 3501 and Cellophane. The aldol condensation process of acetone was monitored using the HPLC-ES-MS technique, and modified PP membranes were evaluated by FT-IR and SEM measurements. With the above-mentioned membrane as a separator, nickel–cadmium cells showed good high-rate performance.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Polypropylene membrane; Nickel–cadmium cell; Acetone oligomerization; Electrochemical properties

1. Introduction

Microporous polypropylene (PP) membranes are used in a variety of industrial applications, as they are one of the cheapest polymer membranes with acceptable thermal, mechanical and chemical stability in commercial applications. One of these applications is electrode separation in alkaline secondary batteries (nickel–cadmium, nickel–metal hydride, silver–zinc). The separator is the smallest (by volume) and the weakest part of the battery and, as a rule, the cycle life of the battery and its performance are limited by separator failure. Although much work has been done on the development of improved separator materials the ideal separator still remains to be developed. The desired separator needs to show the following characteristics: (i) to be a strong mechanical spacing between positive and negative electrodes and have high electronic resistance when submerged

in the electrolyte; (ii) should be as thin as possible for minimum internal cell resistance and maximum cell space for electrodes; (iii) should be chemically resistant to the electrolyte and the active electrode materials; (iv) to be a material with minimum electrolytic resistance (good conductivity in electrolyte) during cell operation; (v) should be manufactured at low cost; other properties rank secondary [1,2].

It must be pointed out that microporous PP membranes could serve as good separators in high-power alkaline batteries; the only problem is the inherent hydrophobicity of PP. To be wetted by an aqueous electrolyte (a concentrated KOH solution) the membrane character needs to be changed to hydrophilic. Although there are several previous reports of treating polypropylene to render its surface hydrophilic, polypropylene has been one of polymers most resistant to chemical modification. The inert nature of polypropylene usually makes it difficult to be chemically modified under mild reaction conditions. In many cases, the reaction involves serious side reactions, such as degradation and cross-linking. Numerous researches have already reported the surface modification of

* Corresponding author. Tel.: +48 61 66 52 152; fax: +48 61 66 52 571.

E-mail address: Aleksander.Ciszewski@put.poznan.pl (A. Ciszewski).



Scheme 1. The proposed procedure of PP hydrophilization and its chemistry.

PP through plasma treatment [3,4], grafting with the use of glow discharge [5,6], corona discharge [7,8], and irradiation with ionizing and UV radiation [9,10]. The advantage of those techniques is the fact that modification usually changes surface properties of the polymer without interfering with the bulk properties simply because of the very low range of their penetration (when the surface-to-volume ratio of material increases significantly, as it does in the case of thin membranes, this is not necessarily true). However, it is well known that an ideal battery separator should be spontaneously, uniformly and permanently wettable in order to accommodate and fully retain the electrolytic solution and to have the lowest possible electrolytic resistance. For these reasons the chosen method of PP modification should create not only the hydrophilic surface of polymer in question but also its bulk—all walls of micropores.

The aim of the present study was to prepare a functional PP membrane that can be used as a separator in a high-power alkaline cell: the nickel–cadmium cell. The general idea for this process is derived from the concept that a hydrophilic PP membrane is really just a hydrophobic polypropylene skeleton, which all pieces are covered by a hydrophilic layer of a modifier. To make the hydrophilic PP membrane we propose a new method consisting in the hydrophobic interaction of the PP skeleton with an amphiphilic substrate to create, by the self-assemble mechanism, a layer of the modifier onto all walls of micropores [11,12]. The novelty of this procedure is that the amphiphilic substrate is not introduced into the structure of the membrane, but is created by a chemical reaction taking place into the pores of the virgin PP and may be treated as a generated paint that will cover all its structure. This chemical reaction in our project is aldol condensation of acetone catalyzed by a base. The whole modified procedure consists of two steps: (i) the virgin hydrophobic PP membrane is saturated with acetone, (ii) the filled membrane is placed into aqueous KOH solution ($d = 1.28 \text{ g cm}^{-3}$), i.e. in the electrolyte typical for the nickel–cadmium cell. This two-part procedure with chemistry of modification is presented in Scheme 1.

Feasibility of the presented procedure is supported by the following facts: (i) acetone and aqueous KOH solution ($d = 1.28 \text{ g cm}^{-3}$) are immiscible liquids; it was checked experimentally, but is not shown in this paper, (ii) aldol condensation of acetone in the base environment is a well documented process [13–17], (iii) products of aldol condensation of acetone are insoluble in applied KOH solution and are confined in the structure of membrane, (iv) acetone disappears from the membrane structure after the process in question and the produced membrane is hydrophilic and filled with the used KOH solution.

2. Experimental

2.1. Materials

Microporous PP membranes (Celgard 2500, USA) were purchased from Hoechst Celanese. Their porosity was 47%, pore

dimension $0.05 \mu\text{m} \times 0.21 \mu\text{m}$ and thickness $25.4 \mu\text{m}$. They were cut into $5 \text{ cm} \times 5 \text{ cm}$ pieces and were cleaned before use through rinsing in methanol for about 24 h, successively washed in distilled water and dried in vacuum, then kept in a desiccator. Acetone and calcium hydroxide were commercial chemicals with analytical purity.

2.2. Modifying procedure

Conditioned hydrophobic PP membrane samples were soaked with acetone at 20°C for 5 min. Successively saturated samples were placed into a 100 ml flask containing aqueous KOH solution ($d = 1.28 \text{ g cm}^{-3}$) at 20°C . After 1 h membranes obtained very low electrolytic resistance and were ready to be used as separators in nickel–cadmium cells.

2.3. Characterization

IR spectra ranging from 4000 to 400 cm^{-1} of virgin and modified membranes were recorded using a Bruker Equinox 55 FT-IR spectroscope. The morphological characteristic of tested samples were observed using field emission scanning electron microscopy (DSM 942 Zeiss-Leo), with samples being sprayed with gold before observation. The process of aldol condensation of acetone was monitored by HPLC-ES-MS using a Waters Alliance 2690 HPLC.

The electrolytic resistance of tested membranes was measured using an experimental cell composed of two compartments. Each had two openings, one for the platinum electrode and one for the Hg–HgO reference electrode. Water tightness between each compartment and the membrane was obtained using two gaskets. The measurements necessary to determine electrolytic resistances of the membrane were performed by potentiometry between two reference electrodes at a fixed current I (A) flowing between platinum electrodes. The membrane electrolytic resistance (area resistance) was determined by two successive measurements of potential difference between reference electrodes; the first one without a membrane, and the second one with the membrane. Aqueous KOH solution ($d = 1.28 \text{ g cm}^{-3}$) was used in all measurements. If a porous membrane is introduced between the reference electrode tips some voltage drop E' is measured (the case without a membrane gives voltage drop E). The membrane electrolytic resistance R was determined from the difference of these two voltage drops (V), according to the following relation [1]: $R = (E' - E)S/I$, where S is the membrane surface area exposed to the electric field (R can be expressed in any convenient units; $\text{m}\Omega \text{ cm}^2$ is frequently used). Each measurement was done in 15 s after switching on the external circuit with fixed current I .

The usefulness of modified membranes for high-power nickel–cadmium cells was evaluated using a model rectangular single vented cell (0.36 Ah, one cathode and two anodes—sintered plates). Discharge characteristics of the tested cell, at different discharge rates, were done at ambient temperature. Prior to record each discharge curve the cell was charged by the constant current charging method. The charge current used

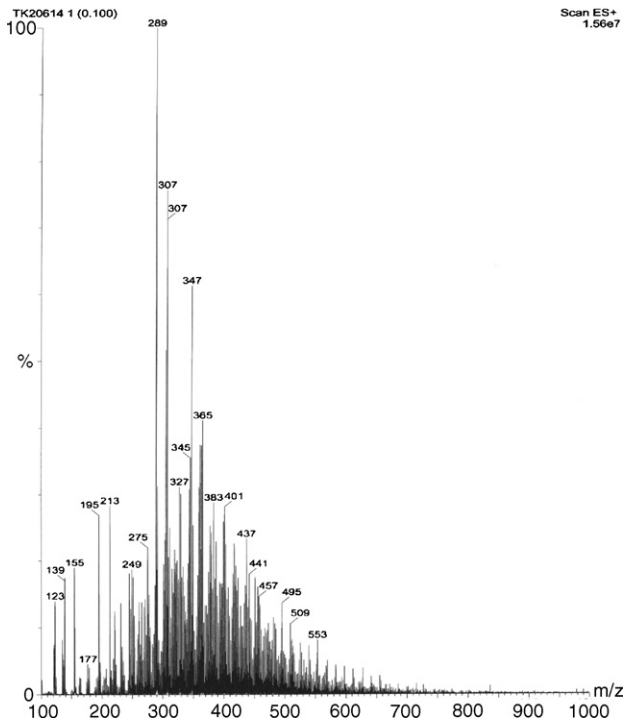


Fig. 1. Mass spectra of the acetone phase after 3 days of contact with KOH solution.

was $0.2C$ (A), where C is the numerical value of the capacity of the cell (Ah).

3. Results and discussion

3.1. Modification

The submersion of the acetone saturated PP membrane into KOH solution starts the aldol condensation process of acetone. It takes place in the closed space, i.e. in the structure of the membrane (in micropores). This process was observed using HPLC-ES-MS in a separate experiment, where two immiscible liquids, i.e. acetone and KOH solution, were in physical contact. Fig. 1 shows ES-MS spectra of the acetone phase after 3 days of contact with KOH solution. A lot of products of the self-condensation reaction of acetone can be distinctly seen, as it could be expected. According to literature data [13–17] the major products of the reaction are diacetone alcohol, mesityl oxide, phorone, mesitylene, isophorone and 3,5-xyleneol and numerous other products are also possible. In turn, Fig. 2 shows a more detailed picture of the process in question; the presented mass spectra were recorded for acetone 1 day after contact of the above-mentioned phases. This picture presents just the representative mass spectra from of a series of measurements recorded from 1 h to 5 days when the process was taking place; all the measurements may not be presented in this short communication. The collected data show that in mass spectra of the acetone phase after contact with KOH solution the highest ion signal intensity was seen for $[M+H]^+$ ions at m/z (99), (121), (139), (157), (179) and (197). It means that the main products of the monitored process are mesityl oxide (98) isomesityl oxide (98), mesitylene (120), phorone

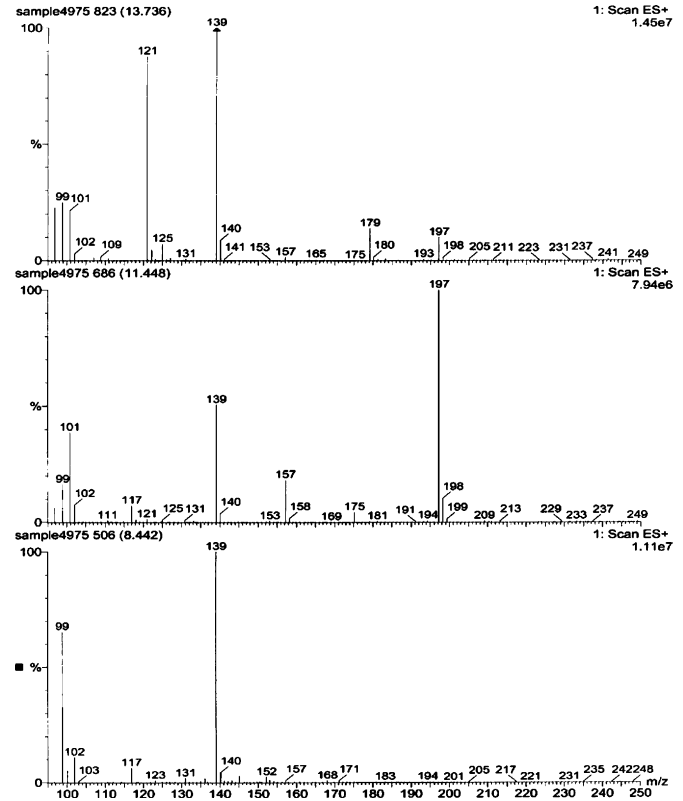
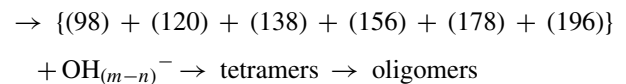


Fig. 2. Mass spectra of the acetone phase after 1 day of contact with KOH solution.

(138), isophorone (138), semiphorone (156), isoxylitone (178) and unknown product ($196 = 138 + 58_{\text{acetone}}$). In compliance with the obtained results the chemistry of aldol condensation of acetone under the examined conditions can be presented as follows:



3.2. Characterization and properties of modified PP membrane

After modification, products of aldol condensation of acetone were anchored on the surface of micropores of the PP membrane, which can be confirmed by FT-IR spectroscopy. Fig. 3 demonstrates the IR spectra of virgin PP and modified PP samples; virgin PP samples exhibited several peaks, which are well matched to those reported in the handbook [18]. It can be seen from this figure that there is an absorption peak around 1700 cm^{-1} in the spectra of modified samples, which cannot be observed for the virgin PP sample. This peak is assigned the stretch of the C=O group. Moreover, due to the stretch of hydrogen bonded with OH groups, a distinct absorption peak can also be seen at 3100 cm^{-1} for modified membranes. These findings confirm the accumulation of unknown aldol condensation products of acetone in the membrane structure.

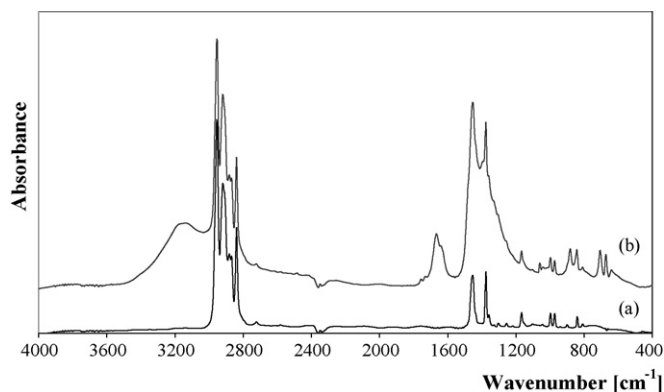


Fig. 3. FT-IR spectra of the virgin PP membrane (a) and modified PP membrane (b).

SEM was applied to compare the change of the surface structure of the original and modified membranes and SEM micrographs are shown in Fig. 4. The figure shows clearly that the original PP membrane has a number of flat or elliptical pores. After modification some pores become smaller and more rounded in shape. It can also be seen that the size of pores in the cross-section of the modified membrane decreased compared with the virgin sample, indicating that the modification also occurred in the deep regions from the surface of membrane due to good wettability of PP by acetone and its subsequent aldol condensation reaction.

To estimate the usefulness of modified membranes as battery separator several properties were measured, namely electrolytic resistance of tested samples and rate performance of 0.36 Ah nickel–cadmium cells with modified membranes as separator.

Table 1

A comparison of electrolytic resistance of tested membranes ($\text{m}\Omega \text{cm}^2$) at different currents

Membrane	Current [A]						
	0.36	1.08	1.80	2.52	3.24	3.96	4.68
Virgin PP				$\geq 100,000$			
mod-PP	25	23	28	29	23	26	24
Cellophane	42	39	44	42	38	47	41
Celgard 3501	32	37	31	38	37	38	32

The electrolytic resistance of examined membranes was presented as a function of current density. This relationship is very important for it shows how the membrane will work in a cell with a different value of discharge current density. Table 1 illustrates this dependence for virgin PP membrane, modified PP membrane (mod-PP) and for comparison commercial membranes: regenerated cellulose membrane (Cellophane) and hydrophilic PP membrane (Celgard 3501). The virgin PP membrane with its hydrophobicity, hence high electrolytic resistance, is totally unsuitable as a separator for alkaline batteries. In contrast, the modified PP membrane reveals excellent behavior even at current density as high as 225 mA cm^{-2} ($3.6 \text{ A} = 10 \text{ C}$), which makes it appropriate for high-power cells. These values turned out to be better than those for cellulose membranes and comparable with those for commercial hydrophilic PP membranes.

The final step of separator characterization was focused on the rate performance of the tested nickel–cadmium cells equipped with a modified PP separator. The rate performance of the cell was evaluated by charging the cell at a constant current of 72 mA (0.2 C) and discharging it at various currents. Fig. 5 presents the

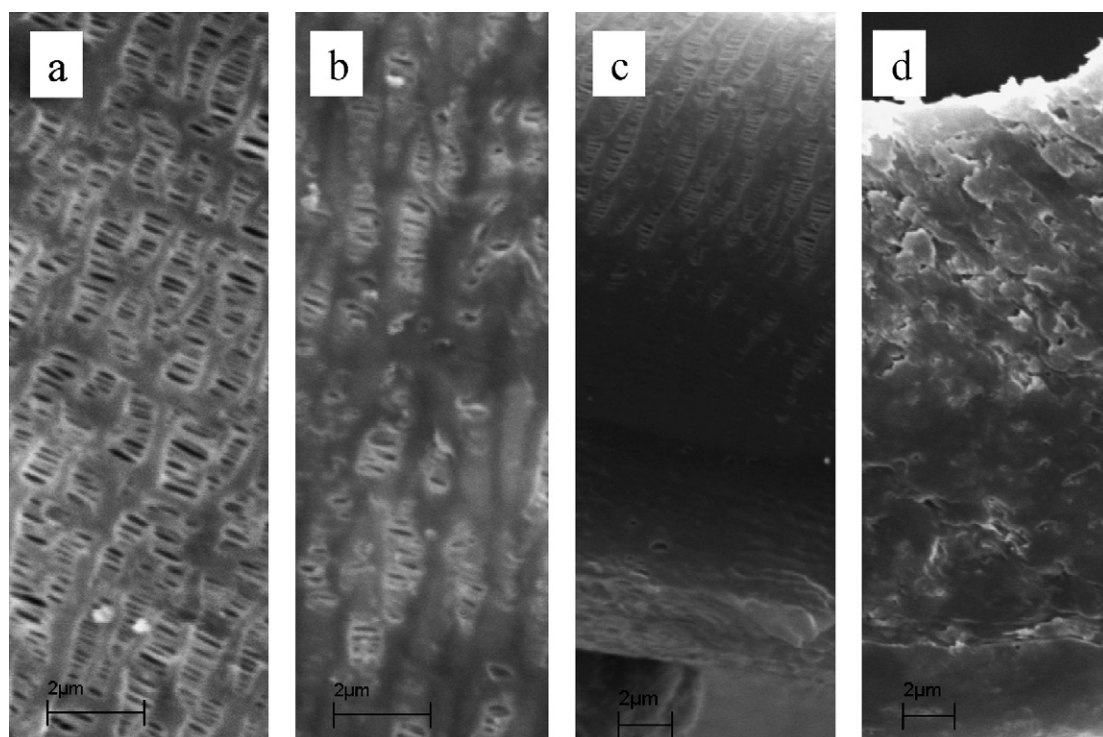


Fig. 4. SEM of surfaces (a and b) and cross-sections (c and d) of the virgin PP (a and c) and modified PP membrane (b and d).

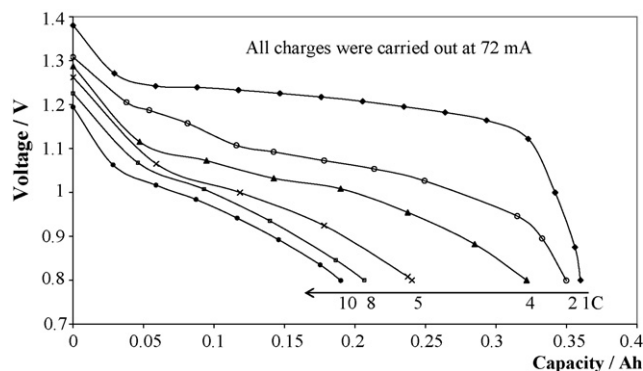


Fig. 5. Voltage–capacity curves of the tested nickel–cadmium cell at various discharge currents, in which numbers show the discharge current.

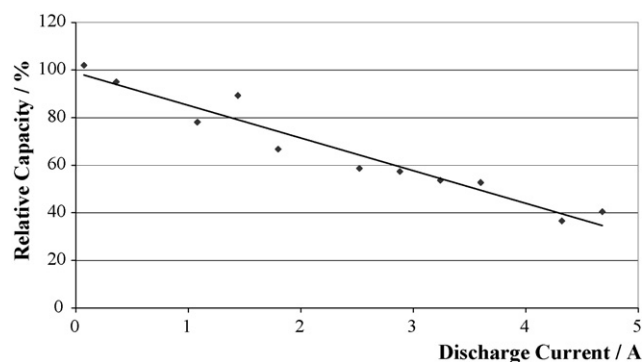


Fig. 6. Correlation of the relative capacity and discharge current for the tested nickel–cadmium cell.

effect of the discharge current on the voltage–capacity profile. It is shown that both capacity and voltage decreased with an increase of the discharge current. This phenomenon is known and can be explained in terms of electric polarization due to an increase in the IR drop. To observe the rate performance, we plotted relative capacity of the cell against the discharge current in Fig. 6, in which the relative capacity is defined as a percentage of the discharge capacity at a specific current to the capacity discharged at 72 mA. It is observed that the cell retained about 60% of relative capacity even as the discharge current increased to 3.6 A (10 C). Moreover, the presented relationship shows that a new modified PP membrane is a good candidate for an inexpensive and safe separator in rechargeable high-power Ni/Cd cells.

The cycle life and stability of modified PP membrane in real working condition, i.e. during repeatedly performed charging/discharging cycles, was determined using the 0.36 Ah cells; charging: 72 mA (0.2 C), discharging: 3.6 A (10 C). This test

consisted of 40 cycles and after each 10 cycles the electrolytic resistance of the membrane was measured. Results obtained in this test ($25 \pm 4 \text{ m}\Omega \text{ cm}^2$ after 40 cycles, $n=5$) prove that modification of the PP membrane is permanent.

4. Conclusions

Summing up, a novel method is reported for the preparation of hydrophilic microporous polypropylene membranes with a relatively low electrolytic resistance under aqueous concentrated KOH electrolyte. We believe that this synthetic strategy will create the possibility for the production of other hydrophilic microporous membranes. Hopefully, it will trigger their application in high-power-area batteries and other fields.

Acknowledgement

The work was financially supported by Poznan University of Technology (BW 31-132/2007).

References

- [1] S.U. Falk, A.J. Salkind, Alkaline Storage Batteries, John Wiley & Sons Inc., New York, 1969, pp. 240–276.
- [2] P. Arora, Z.J. Zhang, Chem. Rev. 104 (2004) 4419–4462.
- [3] B. Bae, B.-H. Chun, D. Kim, Polymer 42 (2001) 7879–7885.
- [4] L. Liang, M.K. Shi, V.V. Viswanathann, J. Membr. Sci. 177 (2000) 97–103.
- [5] U. Vohrer, M. Müller, C. Oehr, Surf. Coat. Technol. 98 (1998) 1128–1131.
- [6] S. Tan, G. Li, J. Shen, J. Appl. Polym. Sci. 77 (2000) 1861–1868.
- [7] F. Seto, Y. Muraoka, N. Sakamoto, A. Kishida, M. Akashi, Angew. Makromol. Chem. 266 (1999) 56–62.
- [8] J. Rahel, M. Simor, M. Cernak, M. Stefecka, Y. Imahori, M. Kendo, Surf. Coat. Technol. 169/170 (2003) 604–608.
- [9] S.-H. Choi, H.-J. Kang, E.-N. Ryu, K.-P. Lee, Radiat. Phys. Chem. 60 (2001) 495–502.
- [10] H. Ma, R.H. Davis, C.N. Bowman, Macromolecules 33 (2000) 331–335.
- [11] B. Rydzynska, Studies on physico-chemical properties of polypropylene membranes as separators in high-power nickel–cadmium batteries, Ph.D. Thesis, Poznan University of Technology, Faculty of Chemical Technology, Poznan, 2006 (in Polish).
- [12] A. Ciszewski, B. Rydzynska, Patent Application P 380,289 (2006, Poland).
- [13] G.S. Salvapati, K.V. Ramanamurty, M. Janardanao, J. Mol. Catal. 54 (1989) 9–30.
- [14] J.I. Di Cosimo, C.R. Apesteguia, J. Mol. Catal. A: Chem. 130 (1998) 177–185.
- [15] A.A. Nikolopoulos, B.W.-L. Jang, J.J. Spivey, Appl. Catal. A 296 (2005) 128–136.
- [16] A.S. Canning, S.D. Jackson, E. McLeod, E.M. Vass, Appl. Catal. A 289 (2005) 59–65.
- [17] G.G. Podrebarac, F.T.T. Ng, G.L. Rempel, Chem. Eng. Sci. 52 (1997) 2991–3002.
- [18] F.C. Pouchert, The Aldrich Library of FT-IR Spectra, vol. 2, 1st ed., 1985, p. 1158.