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COMPOSITES THEORY AND PRACTICE

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# COMPOSITE POLYMER ELECTROLYTES WITH MODIFIED MESOPOROUS SILICA FILLER FOR LI-ION BATTERIES

**Dispersing fine ceramic particles in polymer matrices has proved to be one of the most effective ways of enhancing key structural and electrochemical parameters of polymer electrolytes for rechargeable lithium batteries. It is now widely recognized that the phase composition, morphology and surface chemistry of the filler all exert a clear impact on the way it interacts with the polymer host, thus contributing to the final outcome in terms of ionic mobility, thermal, mechanical, chemical and electrochemical stability in lithium cells. In the present contribution we manufactured microporous polymer membranes based on copolymer poly(vinylidene fluoride-hexafluoropropylene) (PVdF/HFP) using a two-step approach originally proposed by Bellcore. A mesoporous silica filler MCM-41 was synthesized and functionalized with chlorosilane. After the effect of functionalization was verified by means of FTIR spectroscopy, the fillers were incorporated in the polymer matrices and the resulting dry composite membranes showed a well-developed porous structure and a high ability to absorb liquid media with the formation of stable gels. The good physical properties of the membranes were attributed to the enhanced compatibility of the filler with the fluoropolymer matrix. The composite gel electrolytes were prepared by soaking the dry membranes with a conventional lithium cation conducting liquid electrolyte and their electrochemical characteristics were determined in terms of the temperature dependence of ionic conductivity and electrochemical window. During the experimental studies we observed high conductivities at room temperatures exceeding about $2*10^{-3}$ S/cm and decidedly better anodic stability for composite gel electrolytes with an addition of mesoporous silica with and without surface modification.**

**Keywords:** composite gel polymer electrolyte, mesoporous silica, chlorosilane, MCM-41, Li-ion batteries

## KOMPOZYTOWE ELEKTROLITY POLIMEROWE Z MODYFIKOWANYM MEZOPOROWATYM WYPEŁNIACZEM KRZEMIONKOWYM DO AKUMULATORÓW LITOWO-JONOWYCH

**Ciągły rozwój technologiczny, którego konsekwencją jest wzrastająca liczba wykorzystywanych przez nas urządzeń elektronicznych, wymusza poszukiwanie coraz to nowszych rozwiązań konstrukcyjnych i technologicznych chemicznych źródeł prądu umożliwiających ich zasilanie. Akumulatory litowo-jonowe cechują się, jak dotychczas, największą wśród obecnie znanych ogniw żywotnością cykliczną oraz pojemnością w stosunku do ich ciężaru. Jednakże stosowane w nich ciekłe elektrolity organiczne powodują, że akumulatory tego rodzaju nie są w stanie zapewnić odpowiedniego poziomu bezpieczeństwa użytkowania i pojemności ogniw, stąd od kilkudziesięciu lat prowadzone są intensywne badania dotyczące zastąpienia tradycyjnych akumulatorów litowych z ciekłym elektrolitem akumulatorami litowo-polimerowymi, w których ciekły elektrolit zastąpiony zostaje przez elektrolit żelowy czy też polimerowy. Aby umożliwić zastosowanie tego typu elektrolitów w praktycznych układach, stosuje się kolejne modyfikacje prowadzące do poprawy parametrów użytkowych poprzez dodawanie do matryc polimerowych różnego typu wypełniaczy ceramicznych. Przedmiotem naszych badań była charakterystyka fizykochemiczna i elektrochemiczna kompozytowych żelowych elektrolitów polimerowych o różnej budowie matrycy polimerowej i wykorzystaniu do ich wytwarzania wypełniaczy w postaci mezoporowatej czystej krzemionki MCM-41 oraz modyfikowanej powierzchniowo krzemionki MCM-41 z wykorzystaniem chlorosilanu. Badania wykazały znaczną poprawę przewodnictwa właściwego dla kompozytowych żelowych elektrolitów polimerowych, w stosunku do układów pozbawionych wypełniacza, jak również kompozytowe elektrolity polimerowe cechowały się wyższą stabilnością względem anody litowej, co prognozuje możliwość aplikacyjnego ich wykorzystania jako elektrolitów w ogniwach litowo-polimerowych.**

**Słowa kluczowe:** żelowe kompozytowe elektrolity polimerowe, krzemionka mezoporowata, chlorosilan, MCM-41, akumulatory litowo-jonowe

## INTRODUCTION

Lithium-ion batteries have rapidly become the dominant power sources for portable electronic devices, electric vehicles and energy storage systems. The main reason behind their popularity is their high energy density and long life cycle. However, they still cannot be utilized fully because of safety issues. Therefore, the quest for safer and more reliable electrolyte systems is urgent and polymer electrolytes are promising candidates in this regard. The majority of papers concern the use of PVdF and its copolymers as basic polymers of polymer membranes, which are employed as a matrix for gel electrolytes for lithium-ion batteries, because of their advantages such as high ionic conductivity at room temperature, good thermodynamic stability and low requirements for dryness of the environment during battery packing [1-8]. Currently, polymer films are mostly prepared by the phase inversion technique, which is a well-known method for obtaining films with controlled and planned morphology. Taking advantage of this method, we can prepare films that absorb a large amount of liquid electrolyte [9, 10]. Ceramic fillers such as $SiO_2$, $Al_2O_3$, $TiO_2$ were also incorporated along with the host polymer in order to obtain composite polymer electrolytes with improved electrical and mechanical properties [11-13]. The ceramic fillers promote electrochemical properties, but only by physical action without directly contributing to the lithium ion transport process. They can also act as a source of charge carriers when the surface of the ceramic particles is properly modified [13].

MCM-41 material is a mesoporous material known as M41S, which was first reported by Mobil Research and Development Corporation researchers in 1992 [14-18]. MCM-41 is characterized by a one-dimensional, hexagonally ordered pore structure, a high specific surface area and a pore volume of about 1000 $m^2/g$ and 1 $cm^3/g$ respectively, very narrow pore size distribution, a tunable pore size between 1 to 10 nm or more depending on the choice of surfactant, auxiliary chemicals and reaction conditions, adjustable hydrophobicity, and very good thermal stability [14-20]. These properties are of considerable interest to researchers who develop materials for electrochemical power sources [21, 22].

In the present work we synthesized mesoporous silica MCM-41 functionalized with a novel silane coupling agent - dichloro-methyl-octadecylsilane, used as a filler in composite polymer gel electrolytes with PVdF/HFP as the host polymer. The major issues in these modifications are focused on improving the physical, chemical and electrochemical properties of composite polymer gel electrolytes which can have a positive influence on the work parameters of lithium-ion batteries.

## EXPERIMENTAL PROCEDURE

Cl-functionalized MCM-41 was synthesized according to the procedure proposed by Beck et al. [16] and modified with chlorosilane (dichloro-methyl-octadecylsilane) (Fig. 1). The structure of the obtained mesoporous material was verified using a small angle XRD technique with a Philips PW1050 diffractometer, and the TEM technique. The effectiveness of the surface functionalization was examined with an ATR-FTIR spectrometer (Bruker, TENSOR 27).

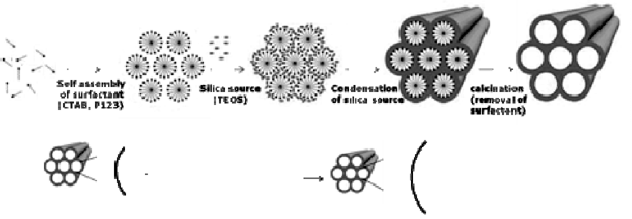

Fig. 1. Scheme of synthesis and modification of mesoporous silica MCM-41 with chlorosilane

Rys. 1. Schemat syntezy MCM-41 i jej modyfikacji z wykorzystaniem chlorosilanu

Dry PVdF/HFP membranes were manufactured using a method similar to the one originally proposed by Bellcore [23]. The PVdF/HFP copolymer (Kynarflex, Atofina) was added to acetone together with dibutyl phthalate (DBP) and the filler powder. The weight ratio of the filler to copolymer was 1:10. The mixtures were stirred vigorously for several hours followed by ten minutes of ultrasonic shaking to prevent aggregation of the filler in the membranes. The solutions were cast on a glass plate covered by a Petri dish and left for the solvent to evaporate slowly. The resulting plasticized membranes were subsequently immersed in diethyl ether, left overnight and stirred to extract DBP. The extraction stew was then dried at 60°C under vacuum. The dry membranes were subjected to SEM observations (cross-sections were obtained by freezing specimens in liquid nitrogen and fracturing). To determine the solvent uptake ability, round pieces cut from carefully dried membranes were weighed and immersed in a container with propylene carbonate (PC, anhydrous, 99.7%, Aldrich). After predefined amounts of time, the membrane pieces were removed from the container, blotted lightly to remove excess liquid, weighed and immediately returned to the container. The liquid phase uptake recorded an increased membrane weight because of membrane swelling: membrane weight increase = $(m_t - m_0) \cdot 100\%$, where: $m_0$ - weight of dry membrane, $m_t$ - weight of membrane after a given time of swelling. The composite gel electrolytes were prepared by immersing round pieces (10 mm in diameter) of dry membranes for 1 hour in an electrolyte consisting of a 1 M solution of $LiPF_6$ (99.99%, Aldrich) in a 1:1 w/w mixture of ethylene carbonate (EC, anhydrous, 99%, Sigma-Aldrich) and dimethyl carbonate (DMC, anhydrous, 99%, Sigma-Aldrich). This is referred to as activation of the dry membranes. Conductivities were determined in two-electrode Swagelok-type cells with stainless steel electrodes at several temperatures (10÷60°C) on the basis of impedance spectra obtained by means of a PARSTAT 2263 (Princeton Applied Research) impedance analyzer in the frequency range of 100 kHz÷1 Hz. Typically, each measurement was repeated several times to ensure good reproducibility of the results. The cells were thermostated during the measurements in a climatic chamber (Vötsch). Anodic stabilities were studied in the Li│gel electrolyte│Pt cells by means of the linear sweep voltammetry technique (scan rate 10 mV/s, potentials swept from rest potential up to 6 V vs. Li/Li$^+$, PARSTAT 2263 (Princeton Applied Research)).

## RESULTS AND DISCUSSION

Figure 2 presents the ATR-FTIR spectra for the mesporous silica fillers. Vanishing of the peak related to –OH (silanol) groups proves that the silane coupling agent bonded with the silica surface. In addition, peaks corresponding to C-H vibration appeared on the spectrum recorded for MCM-41<Cl>. Moreover, the hexagonal pore structure and pore diameter characteristic of mesoporous silicas were confirmed by TEM photography, as shown in Figure 3. We treat the collected data as evidence that chlorosilane-modified mesoporous silica was successfully obtained.

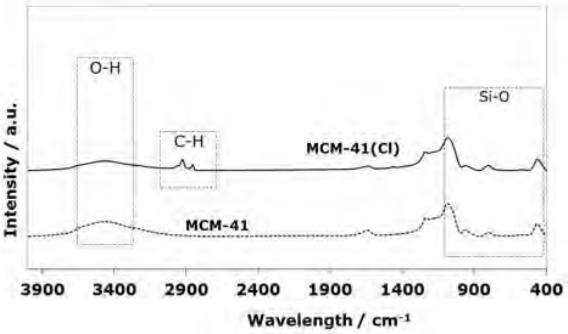

Fig. 2. ATR- FTIR spectra of pristine and Cl-modified MCM-41

Rys. 2. Widmo ATR-FTIR czystego i modyfikowanego MCM-41

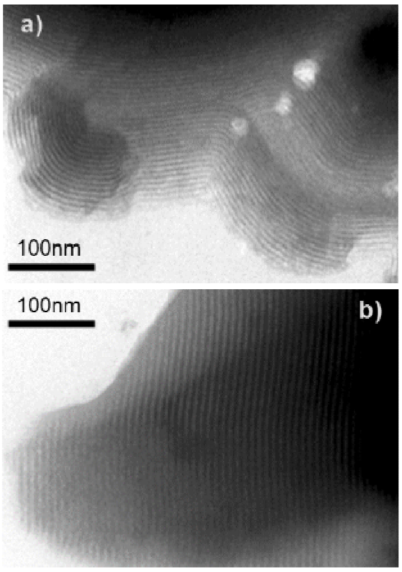

Fig. 3. TEM images of morphology structure of: a) MCM-41, b) MCM-41<Cl>

Rys. 3. Zdjęcia TEM struktury krzemionek: a) MCM-41, b) MCM-41<Cl>

Figure 4 shows the crystallinity change in the composite polymer electrolyte consisting of PVdF/HFP with 10% MCM-41 and PVdF/HFP with 10% MCM<Cl> by X-ray diffraction. The characteristic diffraction peaks of crystalline PVdF are apparent between 20-25 (2 Theta). The crystallinity of the co-polymeric matrix was eliminated after mesoporous fillers were added. Notice that the PVdF crystallinity in the copolymer matrix is not completely reduced after adding a filler, although characteristic small diffraction peaks coming from the crystal domains of PVdF vanish in a high proportion as a result of MCM-41 and MCM-41<Cl> dispersion. A similar phenomenon was reported in our previous paper for PVdF/HFP-based gel electrolytes and for PEO-based polymer electrolytes [23, 25-27].

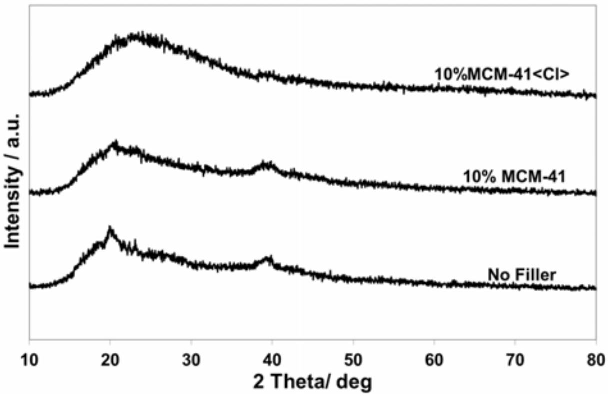

Fig. 4. XRD patterns for membranes without filler and with 10% of pristine and Cl-modified MCM-41

Rys. 4. Dyfraktogram rentgenowski membran polimerowych czystych oraz z 10% dodatkiem: MCM-41, MCM<Cl>

The preparation of PVdF/HFP membranes with both mesoporous fillers is described in the experimental section. Figure 5 presents the SEM images of their cross-sections. Membranes without any filler, which is a consequence of its solid homogenic structure, are presented for comparison. Mesoporous fillers have a dramatic effect on the membrane internal structure, which becomes highly porous, especially compared to membranes without any fillers. The homogeneity of the filler distribution is also quite satisfactory. It was observed that adding mesoporous fillers, both modified and unmodified, enables the manufacture of very high quality composite membranes, which was also observed in our previous work [25-27].

One of the most important parameters of the dry membranes is that they are able to absorb liquid phases and form gels. Figure 6 illustrates how the membrane weights increase when immersed in propylene carbonate. The curves inform us how the masses of the dry membranes increase in time when immersed in the solvent and what the maximum solvent uptake is by a membrane. The membrane without any filler absorbs the least amount of solvent (membrane mass rises by ca. 140%), which agrees with its low porosity, as observed in our other research work [27].

We noticed that all the membranes with a mesoporous filler absorb solvent extremely well and much better than the membrane without any filler. Adding a mesoporous filler to the polymer membrane matrix increases solvent absorption up to 350% of the mass of the dry membrane. The advantage of MCM-41, both modified and unmodified, is clearly visible. Quite surprisingly, the presence of the functionalized mesoporous silica MCM-41<Cl> in the composite polymer membranes does not increase the absorption capabilities compared to the composite membranes with the purine MCM-41 filler, but still the amount of liquid phase is almost twice as high than for 100% PVdF/HFP polymer membranes. Such a good performance in terms of solvent uptake must be attributed to the very well developed internal porosity induced by the examined fillers.

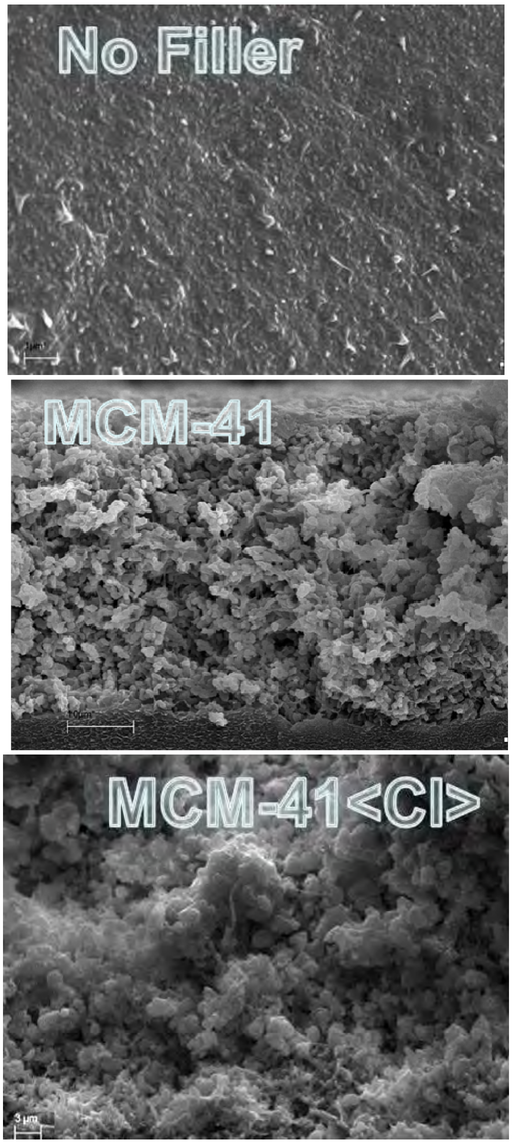

Fig. 5. SEM images of cross-sections of dry membranes containing studied fillers

Rys. 5. Zdjęcia SEM struktur topograficznych suchych kompozytowych membran polimerowych zawierających dodatek badanych wypełniaczy

The ionic conductivity of the PVdF-HFP based composite gel polymer electrolyte is calculated from the equation $\sigma = L/(R_b \cdot A)$, where $L$ and $A$ represent the thickness and area of the electrolyte specimen, respectively. $R_b$ is the bulk resistance of the gel electrolyte obtained from complex impedance measurements.

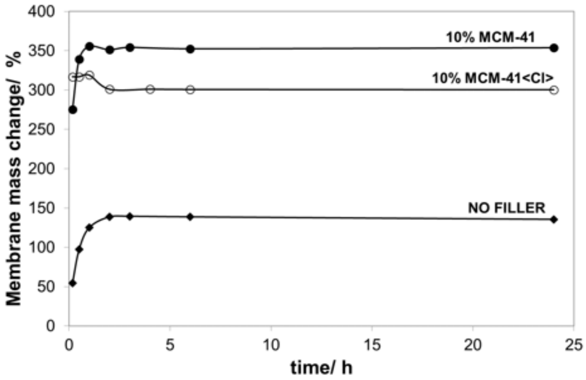

Fig. 6. Solvent uptakes measured for examined dry membranes as function of time immersed in liquid

Rys. 6. Zdolności absorpcyjne badanych kompozytowych membrane polimerowych

Figure 7 shows the conductivity (log $\sigma$) vs. temperature inverse plots of the composite gel polymer electrolyte system without any filler and with additives after and before the mesoporous silica was modified. From the Figure it can be observed that the conductivity versus temperature behavior of the system is linear. Gels containing the functionalized mesoporous filler exhibit the highest conductivities approaching $1 \cdot 10^{-3}$ S/cm$^{-1}$. They were measured for gels with a modified filler in the temperature range of 10÷25°C. From room temperature up to 70°C, the value of conductivity for the composite gel polymer electrolyte is similar for both the composite polymer electrolytes.

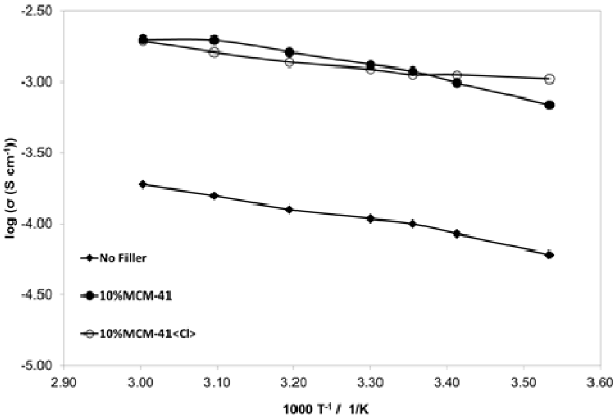

Fig. 7. Temperature dependencies of ionic conductivities determined for gel electrolytes with various fillers presented as Arrhenius plots

Rys. 7. Temperaturowa zależność przewodnictwa właściwego ( krzywa Arrheniusa) żelowych kompozytowych elektrolitów polimerowych zawierających badane wypełniacze mezoporowate

Anodic stability defines an electrolyte's resistance against anodic oxidation (overcharging) in a battery, so it can be classified as one of the most important electrochemical parameters of materials designed for lithium-ion batteries. Figure 8 shows linear sweep voltammetry curves recorded for the studied gel electrolytes using a platinum electrode. All the gels were practically stable up to about 4.5 V. Rapid anodic decomposition could be observed starting from about 4.8 V for the composite electrolyte with the functionalized mesoporous filler. However, after the value of ca. 5.3 V was exceeded, the gels with pristine MCM-41 and without any additions were less resistant to anodic oxidation.

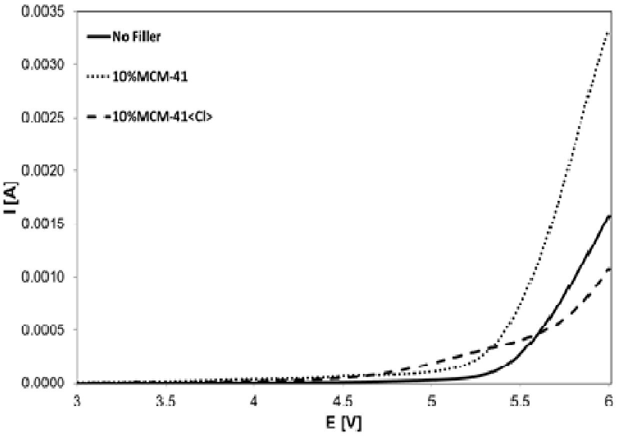

Fig. 8. Linear sweep voltammetry curves recorded on platinum electrode for gel electrolytes with examined fillers

Rys. 8. Krzywe woltametrii liniowej dla kompozytowych żelowych elektrolitów polimerowych z dodatkiem badanych wypełniaczy ceramicznych

## CONCLUSIONS

The paper discusses a new type of filler for polymer gel electrolytes. It also reports the synthesis, structural properties and preliminary electrochemical results for a functionalized mesoporos filler whose surface was modified using chlorosilane. The materials were applied as ceramic fillers in composite polymer gel electrolytes based on PVdF/HFP matrices. It was confirmed that the presence of ceramic filler greatly affects the porous structure, crystallinity and thermal behavior of the polymer matrix. It was also found that surface modified MCM-41 with a chlorosilane agent raises the conductivity of the resulting composite gel electrolytes in the temperature range of 10÷25°C (~$10^{-3}$ S/cm) compared to composite gel electrolytes without filler or with a pristine MCM-41 mesoporous silica addition. The composite gel electrolytes also showed better anodic stability vs. an $Li/Li^+$ electrode compared to gels without additives or with a mesoporous filler without modification.

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