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Abstract

This paper presents synthesis and characterization of polypyrrole based conducting polymers in terms of electronic and mechanical disciplines. Using the electrochemical polymerization approach, conducting polymer samples with different dimensions (length, width, and thickness) was fabricated. For each sample, both sinusoidal and step excitations were used to study its mechanical and electrical properties. An equivalent electric circuit based on constant phase element (CPE) is proposed to model such responses. Electrochemical impedance spectroscopy (EIS) method was used to identify the relationship between the dimensions of conducting polymers and model elements parameters.

Keywords

Synthesis, Modeling, Characterization, Conducting, Polymers

Disciplines

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Synthesis, Modeling and Characterization of Conducting Polymers

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ABSTRACT

This paper presents synthesis and characterization of polypyrrole based conducting polymers in terms of electronic and mechanical disciplines. Using the electrochemical polymerization approach, conducting polymer samples with different dimensions (length, width, and thickness) were fabricated. For each sample, both sinusoidal and step excitations were used to study its mechanical and electrical properties. An equivalent electric circuit based on constant phase element (CPE) is proposed to model such responses. Electrochemical impedance spectroscopy (EIS) method was employed to characterize conducting polymer responses, where nonlinear least squares fitting method was used to identify the relationship between the dimensions of conducting polymers and model elements' parameters.

Keywords: Conducting polymer, electrochemical, synthesis, electrochemical impedance spectroscopy (EIS), nonlinear least square fitting, characterization

1. INTRODUCTION

Conducting polymers (CPs) were invented in the late 1970s because of the crucial accidental discovery of the conductive property of polyacetylene doped with iodine^{1,2}. Since then, conducting polymers have been attracting many scientists to develop a great deal of technological innovations. These polymers are characterized by responsive mechanical, electrical, electronic, magnetic, and optical properties³. Of these materials, the most common and important polymers are polypyrrole (PPy), polythiophene (Ph), polyacetylene (PAC), polyphenylene (PPN) and poly (phenylene vinylidene) (PPV). In this study, the conducting polymer sensor is based on polypyrrole (PPy) – PPy monomers were converted into polymers through a series of electrochemical reactions and then these polymers were deposited onto platinum-coated porous membrane to obtain our conducting polymer “sensor”. Conducting polymer strain sensors are an innovative sensor derived from CPs. An exciting phenomenon is that when DC voltage is applied to the CP beam, it can bend significantly. Later, through a great deal of experiments it has proved that this process is reversible that bending of CPs beam can induce current/voltage. When force was applied to the CP “sensors”, an induced voltage was detected from the electrode probe. Since then conducting polymer sensor as deformation or displacement sensors have been attracting considerable interests in recent years because of its unique mechanochemoelectrical transduction properties.

Conducting polymers can be synthesized using either chemical or electrochemical methods from monomers to CPs. Of the two approaches, electrochemical polymerisation is usually preferred because it provides better control of film thickness. So this type of method is preferred here. Generally, electrochemical polymerisation process involves formation of the radical X^+ , cation of the monomer in the initial stages and this reacts with other monomers in solution to form oligomeric products and then the polymer^{3,4}. The synthesis and doping of the polymer on the substrates are generally implemented nearly at the same time. The A^- , anion is integrated into the polymer to neutralise the charge of the CP film. A mechanism of pyrrole electropolymerisation involving four different steps was presented by John and Wallace⁵. It has been reported that experimental conditions such as monomer substitution⁶, dopants⁶, solvent^{7,8}, pH⁹ temperature¹⁰ and polymerisation methods^{7,11} have a strong influence on the electro-polymerisation process and the properties of the CPs produced. Thus, control of all of these factors is crucial to obtain CPs with desirable properties.

CPs' physical structures are investigated as shown in Figure 1. Each of the elements has their physical meanings, respectively: C_F is Faradic capacitance of the system, R_e and R_i are electronic resistance and ionic resistance, and R_s is solution resistance¹². Ideally, the CP sensors can be regarded as an “energy convert and transfer system”, which turns the chemical energy (due to displacement or bending of the CP sensors) into voltage-potential energy and transfer it by

moving the electrons along the CPs, whose behavior is like electric circuits. So from the view of energy, it is reasonable that electric circuits are determined for the CP sensors behavior. Generally, there are two types of LRC circuits: series and parallel circuits. However, only the parallel one can reasonably be consistent with the physical structure of CP sensors. Thus, it is reasonable to use electric circuits as a system model of CPs.

However, practical CPs sensors show strong nonlinearity, the simple LRC electric circuits cannot precisely describe the behavior of CPs as expected. The EIS is so powerful to analyze electrochemical attributes of electrochemical systems. Therefore, using EIS is one of main tasks in the study¹³⁻¹⁵. Several elements or components are justified through EIS. Double layer capacitance, electrode kinetics (transfer resistance), diffusion layer and solution resistance contribute to the system's EIS spectrum mostly. The "double layer capacitor" on real cells often behaves like a CPE (constant phase element), not a capacitor. After predicting the possible system elements these elements will be built together into an equivalent circuit model. Thus, the arrangement of the element in different combinations will be very important to the system's behavior.

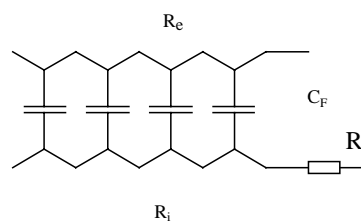


Figure 1 Physical structure of polypyrrole

2. EXPERIMENTAL

2.1 Sample synthesis and preparation

All laboratory chemicals are from the Intelligent Polymer Research Institute (IPRI) of University of Wollongong. They include Tetra Butylammonium Hexafluorophosphate (TBA·PF₆), Pyrrole and Propylene Carbonate (PC) solution to dissolve the TBA·PF₆. The container is a glass beaker with a plastic separator inside allowing the sufficient contact between the electrolyte and the sample substrate. Also, the plastic can fix the anode (sample substrate) on the internal wall of the container. The schematic diagram is shown in Figure 2a. The galvanostat is used for power supply. The thickness of polypyrrole is proportional to the applied current per m² and the time for growing. Before being placed in the fridge N₂ is purged through the solution to remove the O₂. The anode substrate consisted of platinum coated porous poly (vinylidene fluoride) membrane. Polymerisation was conducted at -25°C, as shown in Figure 2b. The current was kept constant and the samples with the different thickness are obtained by changing the time for growing (the period for reactions).

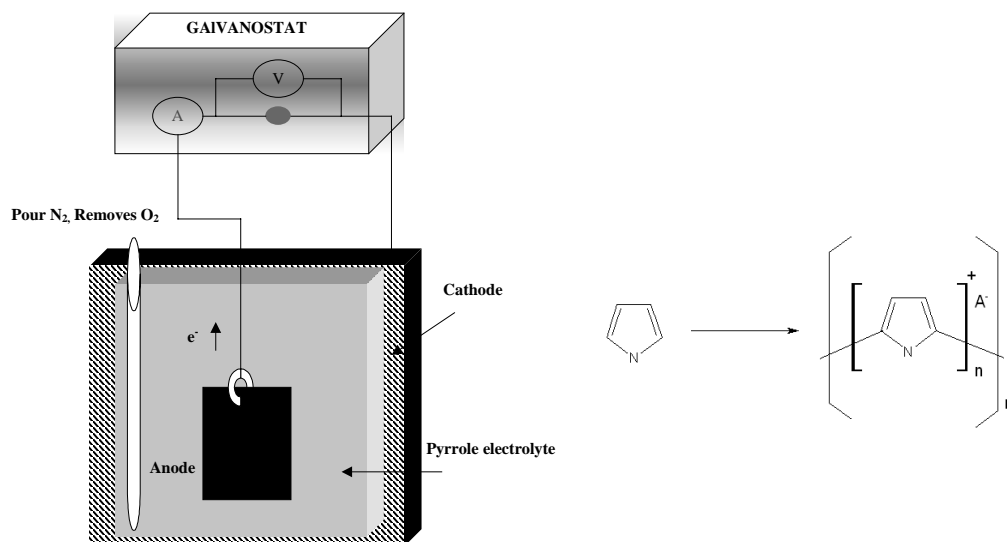


Figure 2 (a) Fabrication of polymer samples (b) reaction in the experiment

2.3 EIS experiment

EIS method is widely used in many areas, especially identification of characteristics of unknown electrochemical systems. The concept of impedance is extended for electrical theory for practical complex electrical circuits, like resistance. It is a measurement of ability of a circuit to resist the flow of electrical current. Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell¹⁶. One feature of this technique is powerful for analysis of complex electrochemical systems. In EIS, an electrochemical cell's complex impedance over a range of AC frequencies can be measured. Several special elements, like CPE, and their characteristics contribute to the system's EIS spectrum. Sinusoidal potential excitation is applied on the CP samples in IPRI. The data for calculating the CPs' impedance are downloaded directly into a computer center through the A/D instrument. The software of Zview can provide the fitting results automatically.

3. RESULTS AND DISCUSSION

Two representative cases of the external dynamic displacement, sinusoidal and step excitations are assumed to be loaded on the tip of the polymer sensor, and the corresponding responses of the sensor are obtained. In general, sensitivity and operating frequency range are two important factors in evaluating vibration sensors. Operating frequency means the flat frequency response region that is normally much lower than the fundamental resonant frequency of the sensor. The sinusoidal displacement excitation can be used to explore the properties of the sensitivity and operating frequency range of the polymer sensors and for the static analysis of polymer sensor.

3.1 Experiment under frequency sweep mode

For the analysis of sensitivity, sensors are deformed using the sinusoidal displacement inputs with amplitude of input displacement constant and changing the frequency gradually. As shown in the following Figure 5, the output Volts are presented at 10, 1, 0.5, 0.4, 0.3, 0.2, 0.1, 0.05 Hz respectively from left to right. The sinusoidal displacement was controlled at constant amplitude at the sensor free end. As can be seen from this figure, the induced voltage shows an increasing trend with frequency until a critical frequency. Above the critical value, the induced voltage decreases steadily with further increment of frequency.

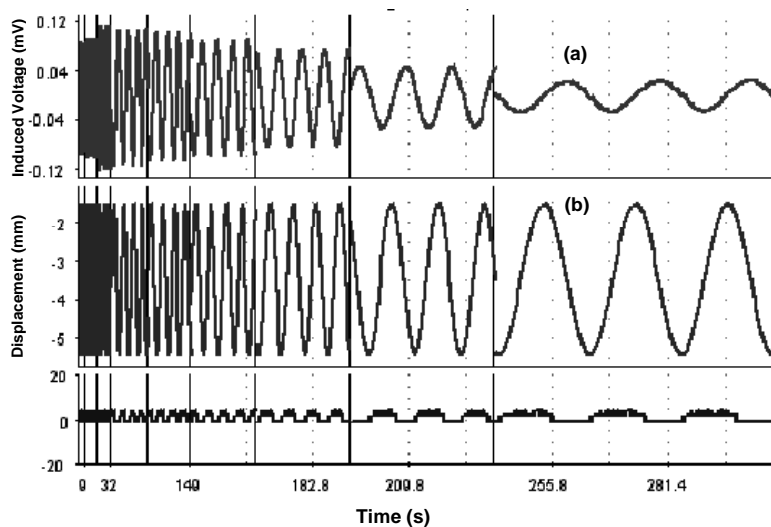


Figure 5 Output voltages at various frequencies

3.2 Experiment under amplitude sweep mode

For the analysis of operating amplitude, the frequency was kept constant and the amplitude was changed regularly. Figure 6 shows the induced voltage versus the displacement amplitudes for a 24H-15mm (time for growing: 24 hour;

dimension: L 15mm) sample. It can be seen from this figure that the induced voltages reach the peak gradually when the displacement increases and then decrease slightly.

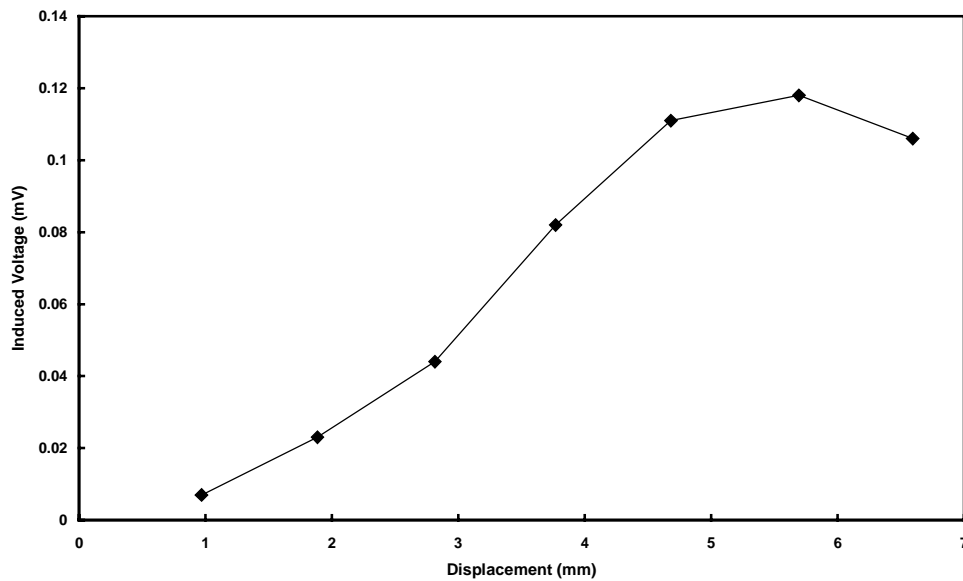


Figure 6 Induced voltages vs. displacement for a 24H-15mm sample

3.3 Effects of polymer sensors under step displacement excitations

As discussed above, the steady-state response of conducting polymers were experimentally studied with sinusoidal excitations with varying amplitudes and frequencies. On the other hand, the dynamic responses of conducting polymers were investigated using step displacement excitations.

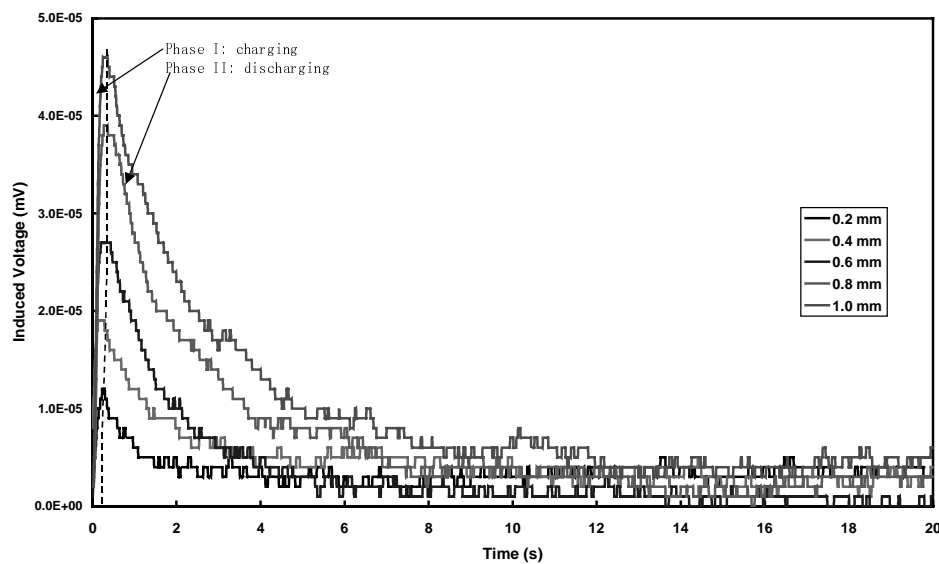


Figure 7 Induced voltages versus step excitation amplitudes

Figure 7 shows time dependence of induced charges of conducting polymers at various step amplitudes of 0.2mm, 0.4mm, 0.6mm, 0.8mm, and 1.0mm. As can be seen from this figure that there are two major processes or phases in the system: system charging and system discharging. The charging phase, phase I, is very short within 0.5 second, which implies that the conducting polymers have good sensitivities for external excitations. This process includes both the reaction transferring chemical energy to electrical potential and charging system using transferred electrical potential. The discharge phase, phase II, is the reverse process of the charging process. Compared with Phase I, this phase takes much longer time to reach steadily. For example, the discharging time for this sample at the 1.0mm step excitation is about 10 seconds.

Basically, the discharging behavior of conducting polymers could be modeled as a first-order RC circuit. However, the results shown in Figure 7 exhibit nonlinear behavior because the discharging time depends on the applied step excitation. As such, simple linear RC circuits cannot precisely describe the dynamic behaviors of conducting polymers.

4. CPE MODELING AND CHARACTERIZATION

4.2 CPE modeling

In this section, a CPE based model is proposed to describe nonlinear responses of conducting polymers, as shown in Figure 8. This model consists of both electrical components and specialized electrochemical elements (CPE). The electrical components R_s , R_i , and R_e represent electrolyte resistance, ionic resistance, and electronic resistance, respectively. The electrochemical elements are used to explain electrode-double-layer-capacitance, electrode kinetics, diffusion layer, etc.

A non-linear least squares fitting program to fit the model to the experimental data was used here. This program attempts to minimize the deviation between the spectrum of the model and the experimental data spectrum. One of the more difficult tasks in equivalent circuit modeling is determining the initial values for the model's parameters. The optimization program needs to start with values (often called seed values) for all parameters. If the initial values are far from the optimal values, the optimization program may be unable to find the best fit. So Matlab's powerful function box is used to obtain the seed values based on the experimental data from step excitation. After obtaining the seeds value of each element, the EIS experiments are used on the exactly the same conducting polymer sensor samples. The software can provide the fitting results automatically. The fitting results are shown in Figure 9. Obviously, the proposed CPE model fits the experimental data very well.

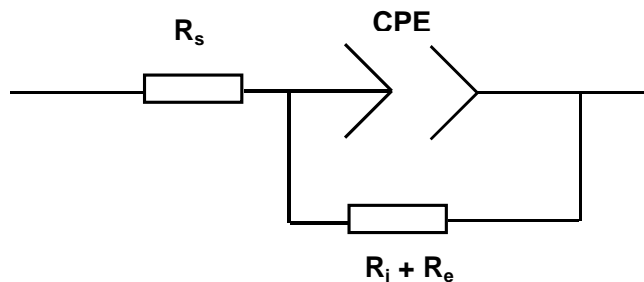


Figure 8 Schematic of the proposed CPE model

4.3 Parameter identification

After the elements of the equivalent circuits model were justified, the other aim of this study is to identify the relationship between the dimensions of conducting polymers and model elements' parameters. The parameters obtained have been used to show that the dimensions of the CPs have effect on the parameters in the circuit models. The following tables' data are the seeds value for the model's parameters. They are calculated using Matlab. The lack of frequency information in the Nyquist format makes it difficult to estimate elements values, especially capacitor. So initial value for fitting parameters was tested in the Bode format. Based on the experimental data from step excitation,

the EIS spectrum in a Bode format is obtained in Matlab. As known, there are three major phases in the wide range of frequencies: Low frequency, middle frequency and high frequency. The electrolyte resistance (R_e) was calculated using information in low frequency; the CPE was calculated in middle frequency; and the R_i and R_s are calculated in high frequency.

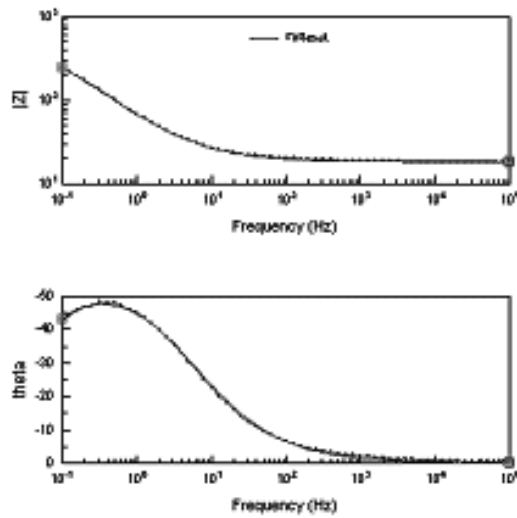


Figure 9 Comparison between CPE modeling predications and experimental results in terms of Impedance magnitude ($|Z|$) and phase angle ($\tan\delta$)

4.4 Summary and discussions

The parameters for various samples are identified and summarized in Table 2 and 3. As seen from these tables, the parameters of the elements of the model are influenced by the sample dimensions, especially the thickness of Conducting polymers. Table 2 shows the results from samples with different thickness. Samples grow for longer times (24hrs) have much thicker layers and show a much larger capacitance. The increase in CPE is from 8.8×10^{-10} (F) to 0.00019 (F) with an increase in growth time from 6 to 24 hrs. The sample length has virtually no effect on the model parameters (Table 3) that had the same thickness. Thus, the double layer formed by chemical reactions (doping) and characterized by the CPE in the model, makes the most contribution to the electrochemical phenomena.

Table 2 Comparison between 24hrs-15mm sample and 6hrs

24hrs-15mm sample	$R_{e1}=10^{-6} (\Omega)$	$R_{es}=10^{-9} (\Omega)$	$CPEe=0.00019 (F)$
6hrs-15mm sample	$R_{e1}=10^{-10} (\Omega)$	$R_{es}=10^{-13} (\Omega)$	$CPEe=8.8 \times 10^{-10} (F)$

Table 3 Comparison between 6rs-20mm sample and 15mm

6hrs-20mm sample	$R_{e1}=10^{-9} (\Omega)$	$R_{es}=10^{-13} (\Omega)$	$CPEe=8.8 \times 10^{-8} (F)$
6hrs-15mm sample	$R_{e1}=10^{-10} (\Omega)$	$R_{es}=10^{-13} (\Omega)$	$CPEe=8.8 \times 10^{-10} (F)$
6hrs-15mm sample	$R_{e1}=10^{-10} (\Omega)$	$R_{es}=10^{13} (\Omega)$	$CPEe=8.8 \times 10^{-10} (F)$
6hrs-10mm sample	$R_{e1}=10^{-10} (\Omega)$	$R_{es}=10^{13} (\Omega)$	$CPEe=8.8 \times 10^{-10} (F)$

5. CONCLUSIONS

The aim of the paper is to model and characterize responses of conducting polymers based on the application of displacement sensors. Two experiments, sinusoidal and step excitations were used to investigate both steady-state and dynamic responses of conducting polymers. For the sinusoidal excitations, the effects of sweeping amplitudes and frequencies on the induced voltages were investigated. At low amplitudes, the induced voltages showed an increasing trend with amplitude. However, when the amplitude is above a critical value, the induced voltage decreases slightly with further incensement of amplitude. Similar results were found in the frequency sweep experiments. For the step excitations, the responses of conducting polymers were classified as two phases: charging phase and discharging phase. The charging phase was very short within 0.5 seconds, while the discharging phase was very long. These results demonstrated that conducting polymers exhibit nonlinearity and could not be modeled with linear RC circuits. As such, a CPE based electric circuit was proposed to describe nonlinear responses. The comparison between the model-predicted parameters and experimental results demonstrated that this model could fit the experimental data very well. Furthermore, the identified results indicated that the sample thickness rather than sample length played an important role in sample responses.

REFERENCES

1. Shirakawa, R. & Chiang, C. K. & Fincher, C. R. & Park, Y. W. & Heeger, A. J. *et al.*, *Phys. Rev. Lett*, 1977, 39, 1098
2. Shirakawa, H. & Louis, E.J. & MacDiarmid, A. G. & Chiang, C.K. & Heeger, A. J., *J Chem. Soc., Chem. Commun.*, 1997, 578
3. Raymond, D. E. & Harrison, D. j., *J. Electroanal. Chem.*, 1993, 361, 65
4. Sadki, S. & Schottland, P. & Brodie, N. & Sabouraud, G., *Chem. Soc. Rev.*, 2000, 29, 283
5. John, R. & Wallace, G. G., *J. Electroanal. Chem.*, 1991, 306, 157
6. Trivedi, D. C., *Bulletin of Mster. Sci.*, 1999, 22, 477
7. Barisci, J. N. & Liu, L. & Strounina, E. V. & Wallace, G. G., *Colloids & Surfaces Aphysicochem. & Eng. Aspects*, 2000, 167, 201
8. Choi, S. J. & Park, S. M., *J. Electrochem. Soc.*, 2002, 149, E26
9. Davey, J. M. & Too, C. O. & Ralph, S. F. & Kane-Maguire, L. A. P. & Wallace, G. G. *et al.*, *Macromolecules*, 2000, 33, 7044
10. Teshima, K. & Yamada, K. & Kobayashi, N. & Hirohashi, R., *J. Electroanal. Chem.*, 1997, 426, 97
11. Stankovic, R. & Pavlovic, O. & Vojnovic, M. & Jovanovic, S., *Euro. Polymer J*, 1994, 30, 385
12. Xiaoqi Bao, Yoseph Bar-Cohen, Syhyh-shiuh Lih, *Measurement and Macro Models of Ionomeric Polymer-Metal Composites (IPMC)*, Jet Propulsion Lab, California Institute of Technology, 2002
- 13 Gamry Instruments, *Equivalent Circuit Modelling Using the Gamry EIS300 Electrochemical Impedance Spectroscopy Software*, www.gamry.com
14. Gamry Instruments, *Electrochemical Impedance Spectroscopy Primer*, www.gamry.com
15. Rubinstein, I., *Physical Electrochemistry Principles, Methods, and Applications*, 1995, Marcel Dekker
16. Etter, D. M., *Engineering Problem Solving with Matlab*, 1993, Prentice-Hall International