

Chemically modified polymethyl methacrylate in a magnesium-polymer cell

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ABSTRACT

As a result of the electrophilic protonation of a carboxyl group of dielectric polymethylmethacrylate (PMMA) with trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$), a modified conducting polymer material was produced in the shape of a thin elastic lamina and a dense conductive gel, whose density was 1.26 g/cm^3 . These polymers conduct electricity, do not dissolve in either cold or warm water and are also resistant to weather conditions. Their conductivity in room temperature is $7.5 \cdot 10^{-3} \text{ Scm}^{-1}$ and it greatly increases above 154 K. Activation energy E_a decreases with increasing temperature in the range 154 K – 300 K from 1.47 eV to 0.69 eV. The magnesium-polymer (Mg-Poly) cell is constructed with magnesium as the anode and conductive PMMA as the cathode and both electrodes are electrically connected with a polymer gel electrolyte. The rated voltage of this cell is 2.4 V.

Keywords:

Conducting polymer; Electrical property; Polymer battery

1. INTRODUCTION

Pure and solid polymethyl methacrylate (PMMA) is not conductive, but by chemical modification it is possible to obtain a conducting polymer. Conducting polymers by virtue of their electrical parameters and other properties like lightness, flexibility, durability, resistance to corrosion, ductility, non-toxicity and esthetic values have found an application in many electronic devices. Many dissertations have been published about new polymer electrolytes [4-10] since the first publication by Wright [1,2] which were about poly(oxyethylene) including a salt and an announcement by Armand in 1978 [3] who proposed a practical use of conductive polymers in cells. Dissertations dealing with the applications of conductive polymers in electrochemical secondary cells and photoelements used for battery-powered electronic devices are very popular [11,12]. Technological and operational requirements as well as safety considerations during cell production require the usage of polymer electrodes and the replacement of liquid and volatile electrolytes by alternative solid electrolytes. Chemically modified PMMA can be used as a material to make an electrode or the electrolyte of a cell.

2. EXPERIMENTAL

To obtain a polymer electrolyte, a reaction of electrophilic protonation of PMMA carboxyl group with trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$) was performed. Fragmented, pure PMMA dissolved in chloroform (CH_2Cl_2) reacts with trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$) without air access. The reaction is slow and takes 24 hours but occurs at room temperature. The reagents should be stirred every few hours. When the excess of chloroform and acid evaporate we have a brown material which has a dense and transparent gel form. To make a polymer cathode use a 2 mm thick PMMA lamina interacting on the surface of $\text{CF}_3\text{SO}_3\text{H}$ and then proceed as above with the electrolyte. As a result of these operations a polymer cation which is countervailed with triflic nucleophile can be obtained (Fig.1).

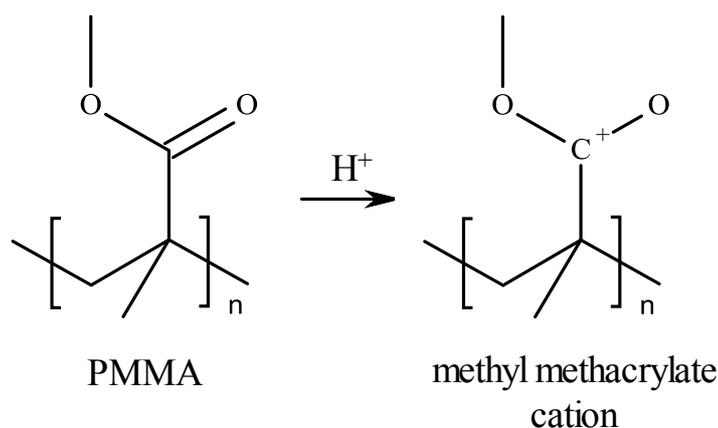


Fig. 1. Electrophilic protonation of carboxyl group of PMMA.

A thin, light, elastic and conductive polymer electrode was obtained. Solubility in warm and cold water, stability under a variety of weather conditions, density, ignition temperature in an open crucible pot of the polymer were determined. DTA (differential thermal analysis) was also conducted. Using an Agilent 4284 A Precision LCR Meter, the conductivity of the received polymer electrode was measured in the bandwidth of 20 Hz – 1 MHz and a voltage of 1V. The temperature was changed from 120 K to 300 K with a step size of 2 K per minute. The precision of the reading was $5 \cdot 10^{-3}$ K. A sample in the form of a 2 mm thick lamina was placed between flat parallel gold electrodes (2.5 mm x 6 mm x 0.05 mm) which were connected with copper wire. The sample was measured in the admittance mode (G-B mode), where G is the conductance and B is the electric susceptability.

Admittance Y is the complex number,

$$Y = G + iB = |Y| \exp(i\Phi) \quad (1)$$

where

Φ is the phase angle,

$$\Phi = \arctan\left(\frac{|B|}{G}\right) \quad (2)$$

The inverse thermal energy dependences (E^{-1}) of the conductivity natural logarithm ($\ln \sigma$) for chemically modified PMMA with $\text{CF}_3\text{SO}_3\text{H}$ at different frequencies of electric field were determined and are expressed in Fig.2.

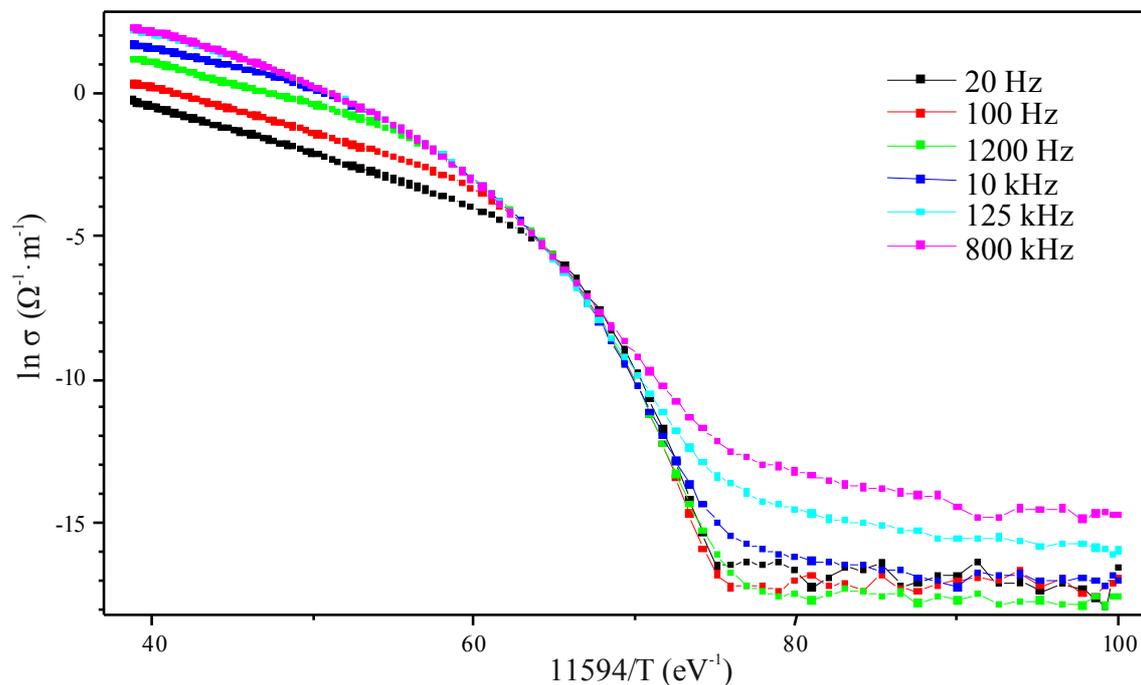


Fig. 2. The inverse thermal energy dependences (E^{-1}) of the conductivity natural logarithm ($\ln \sigma$) for the modified PMMA in the different frequencies of the electric field.

The time dependences of conductance $G(t)$ at the different frequencies of electric field and temperature $T(t)$ for modified PMMA (Fig.3) were tested.

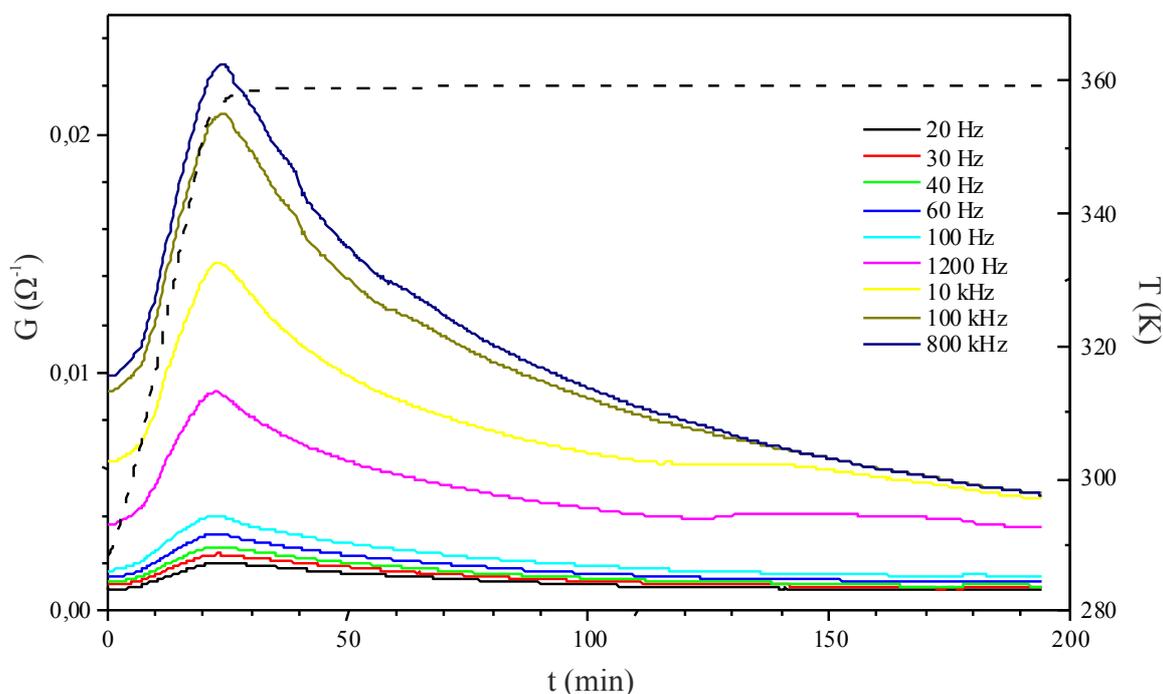


Fig. 3. The time dependences of conductance $G(t)$ for the different frequencies of the electric field at a 360 K for the modified PMMA

The size of the electric current in the circuit without external power was shown in Fig.4.

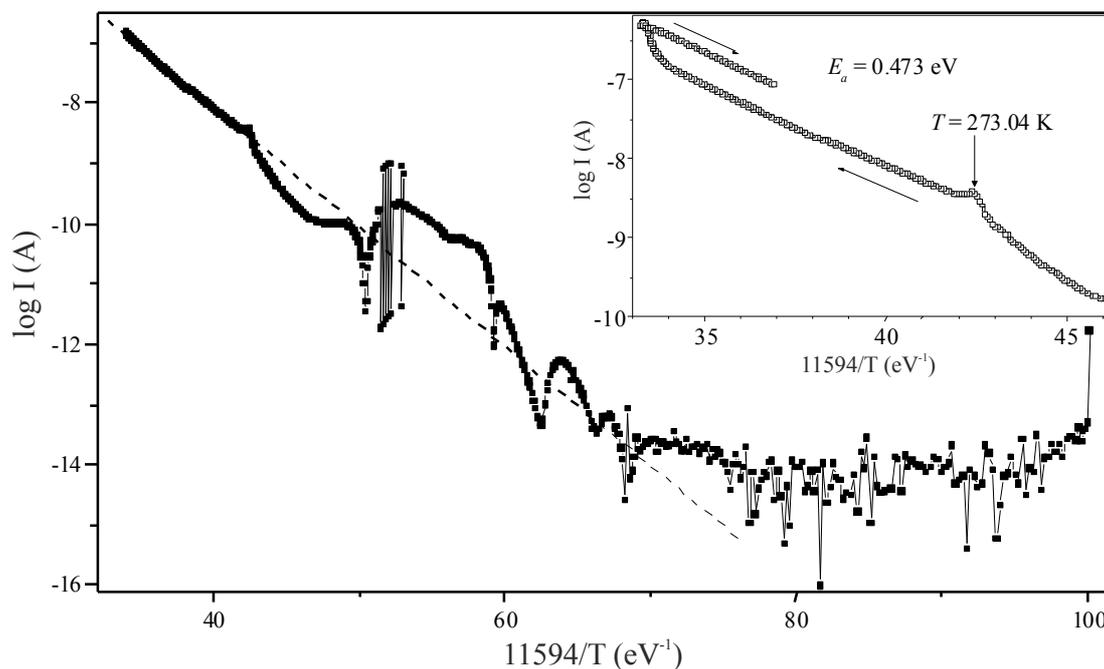


Fig. 4. The inverse thermal energy dependences ($11594/T$) of thermo-stimulated direct current (I) in the modified PMMA. The broken line is the linear approximation of the relation in the range of 165 – 340 K. The insert represents the same relation but for the heated and then the cooled modified PMMA.

Tests using modified PMMA as a cathode or electrolyte at the voltaic cell were also conducted. Then a prototype Mg-Poly secondary cell with magnesium as an anode and modified PMMA as a cathode was constructed. Both electrodes were electrically connected with an electrolyte (chemically modified dense polymer gel). A cellulose flimsy acted as a separator. Next using these materials the battery as pictured in Fig.5 was made, and then the current-voltage properties of the produced cell and battery were tested.

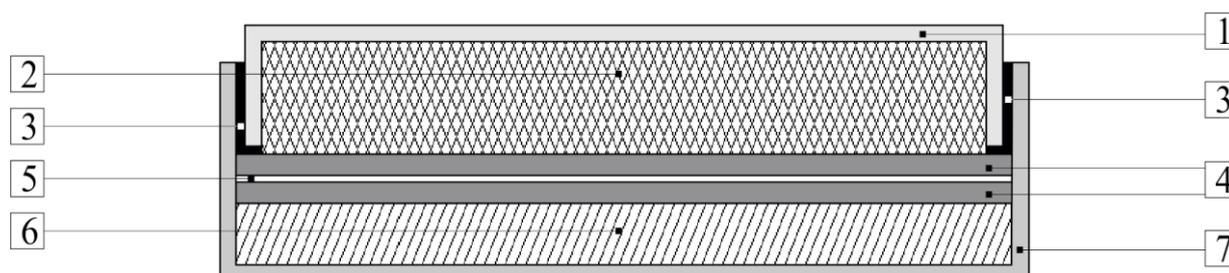


Fig. 5. Diagram example of a single “Mg-Poly” cell: 1 – cathode can, 2 – cathode (conductive PMMA), 3 – insulator, 4 – electrolyte (polymer), 5 – separator, 6 – anode (magnesium), 7 – anode can.

3. RESULTS AND DISCUSSION

Solid and transparent form polymer material and dense, transparent form gel were obtained. The reaction product depends on the PMMA form used in the reaction. Polymethyl methacrylate can be used in a solid or powdered form. Both the reaction products do not dissolve in either cold or warm water and they are also resistant to weather conditions. 48 hours exposure to room temperature with air access does not have any effects on their substantial changes. Above 420 K, modified polymers decompose into carbon and various gas products. The ignition temperature of the modified PMMA is about 560 K.

This PMMA conducts electricity and its conductivity at room temperature is $7.5 \cdot 10^{-3} \text{ Scm}^{-1}$. The inverse thermal energy dependence of conductivity $\sigma(T)$ (Fig.2) is described by the Arrhenius type relation,

$$\ln \sigma = \ln \sigma_0 e^{\frac{E_a}{k_B T}} \quad (4)$$

but not in the whole temperature range, because the relevant values of activation energy are not constant in the whole range. The activation energy E_a in the range 0.69 – 1.47 eV decreases with increasing temperature within the range 154 K to 300 K (Fig.2). The object's conductivity σ at the temperature below 160 K is very low and it acts as an insulator.

However at a temperature above $T > 200$ K it shows the conductive properties. The resulting polymer undergoes temperature-stimulated transitions from dielectric state to conducting state between 150 K and 200 K. Testing polymer below 150 K is possible in a glass-like phase, which characterizes low average drift velocity. Above 200 K it is in a quasi-liquid phase with much higher average drift velocity (Fig.2). Testing the polymer at a 360 K decrease in conductance (G) is observed. Decrease in conductance is also observed with cooling (Fig.3).

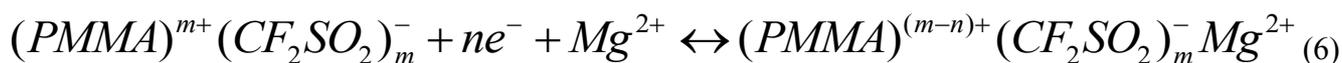
An interesting attribute of the chemically modified polymer is that, while heating without external power, it generates a direct current in the circuit. An increase of electric current from 10^{-14} A commences at a temperature of 155 K (75 eV^{-1}). A quasi-monotonic temperature-dependence of current $I(T)$ in the background of small random oscillations can be observed from Fig.4. The activation energy $E_a \approx 0.5$ eV appropriate to this dependence is located in the range from 155 K to 300 K. The thermo-stimulated current is probably the result of a released electrical charge from bonds during the transition of polymer from solid to quasi-liquid phase. $I(T)$ dependence shows temperature-reversible quality which indicates electret state of modified polymer at the temperature above 155 K (Fig.4).

As a result of these electro-physical properties, the chemically modified PMMA can be used as a polymer cathode and also a polymer electrolyte of voltaic cells. The obtained magnesium-polymer "Mg-Poly" (Fig.5), using magnesium as an anode, the modified PMMA as a cathode, a dense gel form polymer electrolyte and a cellulose separator gives a rated voltage of 2.4 V. Battery ratings made of those three cells have a current of 1800 mAh. Electrode reactions in one cell can be presented as in the schema below:

The anodic reaction of magnesium electrode is:



but the reversible cathodic reaction of the conductive polymer with electrosorption of Mg^{2+} is:



4. CONCLUSIONS

Chemical reaction of dielectric PMMA with trifluoromethanesulfonic acid (CF_3SO_3H) allows the conductive polymer material whose conductivity at room temperature is $7.5 \cdot 10^{-3} \text{ Scm}^{-1}$ to be obtained. The state of the matter, conductivity, chemical stability and other electro-physical properties of the material produced allow the application of the modified PMMA as a cathode and as an electrolyte of voltaic cells. The rated voltage of that single Mg-Poly cell amounts to 2.4 V but the battery current rating comprised of those three cells is 1800 mAh.

References

- [1] D. E. Feton, J.M. Parker, P.V. Wright, *Polymer* 14 (1973) 589.
- [2] P. V. Wright, *Br. Polymer J.* 7 (1975) 319.
- [3] M. B. Armand, J. M. Chabagno, M. J. Duclot, *Fast Ion Transport in Solids* 131 (1979).
- [4] A. Lewandowski, K. Skorupska, J. Malinska, *Solid State Ionics* 133 (2000) 265.
- [5] A. Lewandowski, M. Zajder, E. Frackowiak, F. Beguin, *Electrochim. Acta* 46 (2001) 2777.
- [6] M. B. Armand, *Rev.Mater. Sci.* 16 (1986) 245.
- [7] J. R. MacCallum, C. A. Vincent, *Polymer Electrolyte Reviews 2*. Elsevier, London, 1989.
- [8] H. R. Allcoc, W. R. Laredo, R. V. Morford, *Solid State Ionics* 139 (2001) 27.
- [9] A. A. Mohamad, N. S. Mohamed, M. Z. A. Yahya, R. Othman, S. Ramesh, Y. Alias, A. K. Arof, *Solid State Ionics* 156 (2003) 171.
- [10] N. Kaskhedikar, M. Burjanadze, Y. Karatas, H.D. Wiemhöfer, *Solid State Ionics* 177 (2006) 3129.
- [11] J. Godlewski, *Advances in Colloid and Interface Science* 116 (2005) 227.
- [12] A. M. Elmer, P. Jannasch, *Solid State Ionics* 177 (2005) 573.