Short Communication

Electrochemical capacitor using polymer/carbon composites

J.M. Pernaut*, G. Goulart

Departamento de Química/ICEx CP 702, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, Brazil

Abstract

An electrochemical capacitor fabricated by thin-film techniques is described. The active principle is based on the electrical capacitance of a polymer electrolyte/carbon interface. The flexible multi-coating device (500 μm thick) consisted of a plasticized poly(ethylene oxide) lithium perchlorate electrolyte film, two carbon composite electrodes and large area collectors. The electrochemical and electrical properties of the components and the complete cell are presented. After 5000 operation cycles the device exhibited a maximum capacitance of 2.4 F cm^{-3} providing an energy density of 20 kJ l^{-1} with a peak power about 300 W l^{-1}.

Keywords: Capacitor; Polymer electrolyte; Carbon

1. Introduction

Recent developments in electrical equipment require integrated energy storage systems associating high energy density with short charge time. The electrochemical capacitor using the charging of the electric double layer at the interface of a high porous electrode in contact with an electrolyte could satisfy these criteria [1]. Numerous reports describing this kind of systems are found in the literature, principally using activated carbon as an electrode (paste [2] or clay-composite-type [3]) and conventional [4] or solid-state electrolyte [5].

We report here preliminary results concerning the study of a simple flexible solid-state system based on the use of a polymer electrolyte film, carbon black/polymer composite electrodes and large-area current collectors. The study was performed under ambient conditions with commercially available products.

2. Experimental

Porous nickel electrochemical foils (Fukuda) were used as large-area collectors (C) (10 cm$^2 \times$25 μm). The polymer electrolyte (PE) was composed of a solid mixture of poly(ethylene oxide) (PEO), (Polyox, average mol. wt. of 6$\times$10^5), poly(ethylene glycol) (PEG, Aldrich, average mol. wt. of 400), and LiClO$_4$ (Aldrich). The salt concentration was fixed at [O]/[Li]=8 and the polymer ratio was varied between 1:0 and 1:1. All the products were used as-received. The films were prepared by the conventional solvent casting method on the collector surface using acetonitrile CH$_3$CN (PA grade, Maia, Brazil) as solvent. The calculated film thickness varied from 25 to 100 μm according to the quantity of polymer and salt dissolved. After casting, the solvent was allowed to evaporate under vacuum at room temperature. For the characterization of PE, the films were sandwiched using a second collector foil and a silver strip (1 cm$\times$0.5 cm$\times$25 μm) as a pseudo-reference electrode (SPRE) (Fig. 1(a)) and heated for 30 min at 60 °C. The composite electrodes (CE) consisted of a mixture of the electrolyte with carbon black (CB) powder (Printex XE2, (BET 950 m^2 g^{-1}) content varying from 5 to 25 wt.%. The films (thickness calculated from 100 to 250 μm) were prepared by dissolving, under stirring, the polymer in a solution containing the solvent, the carbon and the salt, followed by evaporation of the solvent under atmospheric pressure at room temperature. The solvent was finally eliminated, as with the PE, and a cell was assembled for characterization as described above. The complete cells (Fig. 1(b)) were made either by building two elements consisting of the C/CE/PE configuration in a first step and then assem-
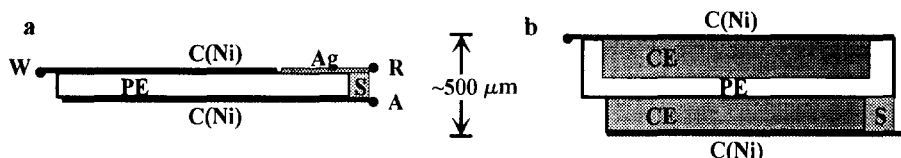
* Corresponding author.

Fig. 1. Schematic view of the (a) electrolyte cell and (b) complete cell (electrochemical capacitor): (C) collector; (PE) polymer electrolyte; (CE) composite electrode; (R, A, W) reference, auxiliar, working electrodes, and (S) separator (insulating film).

bling them, as shown before, for the PE, or preparing two elements consisting of C/CE and using them to sandwich an electrolyte film transferred from a non-adhesive Teflon-based substrate (Bioblock Scientific). The electrochemical and a.c. electrical properties of the partial and complete cells were characterized at room temperature by cyclic voltametry, chronoamperometry, potentiometry and impedance measurements using a universal electrochemical system (Autolab, Echochemie) and a Hewlett-Packard impedance analyser Model 4192A. The electrical parameters were deduced using an equivalent circuit model (B.A. Boukamp). The d.c. electrical measurements were performed with a digital multimeter (Minipa ET-2060). A function generator HP 3310A checked by an oscilloscope MEGURO MO-1252A was used for cycling experiments.

3. Results and discussion

3.1. Study of the polymer electrolyte

Since the capacitor is to be operated with current densities higher than 1 mA cm^{-2}, the potential range for which the faradaic current of the PE did not exceed 10% of this value, i.e., 0.1 mA cm^{-2}, was determined by cyclic voltammetry. A large series of PE films with varying thickness and ratio PEO:PEG were studied. The electrochemical response was relatively constant and independent of the polymer ratio in our potential range. A typical curve obtained in the presence of ferrocene (calibration of SPRE) is presented in Fig. 2. The ferrocene oxidation was not reversible in this medium nor even in pure PEG where a quasi-reversible
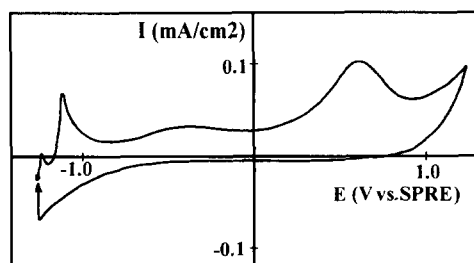

Fig. 2. Cyclic voltammogram (20 mV s^{-1}) of an LiClO$_4$/POE ([O]/[Li]=8) film (~100 μm) in presence of ferrocene; working and auxiliar electrodes = Ni 10 cm^2, and reference electrode = SPRE.

system was revealed. Using platinum as a working electrode in 0.1 M LiClO$_4$/PEG, the standard reversible redox system was obtained at $E^{o'}=0.415$ V which provides the relation $E_{SPRE}=E_{NHE}-0.235$ V. The PE electrochemical stability range according to our criteria reached 2.5 V (−1.25 to +1.25 V versus SPRE) which was satisfactory for our purpose. The cathodic current at −1.25 V was probably due to the reduction of H$^+$ from residual water as suggested by the oxidation of adsorbed-like species on the anodic scan. The oxidation at 1.25 V could involve the oxidation of nickel and/or perchlorate [6]. The a.c. behaviour of the PE films was studied; the low frequency feature was attributed to the double-layer capacitance at the PE/Ni interface, whereas the high frequence resistance was due to the electrolyte [7]. Our results did not prove clearly the relation between the proportion of PEG and the resistance probably because of the contribution of water in the conduction process. Nevertheless, high values of conductivity estimated between 10^{-5} and 5×10^{-5} S cm^{-1} were obtained in our working conditions. The double-layer capacitance was found to be 50 μF cm^{-2}, in agreement with the porous nature of the interface.

3.2. Study of the composite electrode

The ratio POE:PEG = 3:1 was used because it allowed the incorporation of a high fraction of carbon without the occurrence of segregation in the composite; it provided a good compromise between conductivity and mechanical cohesion of the PE. The impedance behaviour of CE (between 1 MHz and 1 mHz) as a function of the carbon-black fraction in the composite (5 to 25 wt.% CB) was analysed. All the spectra had a $R_{HF}(R_cC_c)$-type response. The total resistance R_t ($R_t=R_{HF}+R_c$) characterized at low frequency (10^{-2} Hz) was mainly electronic since it was equal to the static d.c. resistance within a 10% range error. The value of R_t decreased with the fraction of carbon in a percolation transition-like form (see Fig. 3) whereas the associated parallel capacitance, C_c, remained roughly constant within the uncertainty range. In a first approximation this behaviour can be described by the carbon–plastic composite model [8] where C_c is the contact capacitance and R_c the contact resistance between the conducting aggregate. The high frequency R_{HF} resistance would represent the resistance within
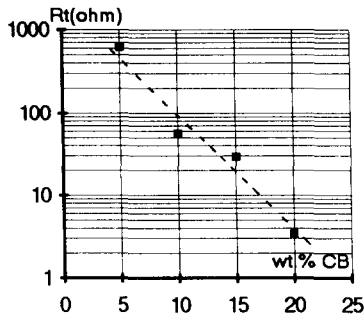
Fig. 3. Evolution of the electrical resistance R_t of the CE films (~150 μm) sandwiched between two nickel collectors, 10 cm^2, as a function of the carbon-black content (wt.% CB). R_t is obtained from impedance measurements at 10^{-2} Hz or by d.c. measurements.
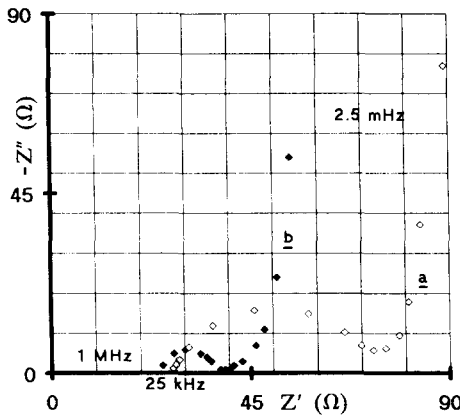

Fig. 4. Complete cell Ni//CE/PE/CE//Ni (10 cm^2 area, ~450 μm thickness, PE = POE:PEG (3:1), [O]/[Li] = 8). Impedance diagram is applied at 0 V: (a) 15 wt.% CB, few cycles, and (b) 20 wt.% CB, ~1000 cycles.

the aggregate with a possible ionic contribution at low carbon content.

3.3. Study of the complete cell (electrochemical capacitor)

The characteristics of the cells were studied by different dynamical methods between −2 and +2 V at various degrees of cycling (from 1 to 5000 cycles), which consisted of charging/discharging the cell by applying respectively 1 V for 5 min and 0 V for 5 min (50% charge depth). The complete impedance response of the cells is presented in Fig. 4 at 0 V; no significant change of the features was detected between −2 and +2 V. The global behaviour included the electrical contribution of the two CE and the PE elements, plus a diffusive limitation for the higher carbon content case. The high frequency resistance (electrolyte) did remain constant in all cases and the sum of the resistance of the two CE in the semi-circle ($2R_c$) was identified for the lower carbon contents. The equivalent capacitance determined at low frequency was 0.6 F (1.3 F cm^{-3}) and 1 F (2.2 F cm^{-3}) for 15 and 20 wt.% CB,

respectively and the value of the associated serial resistance was 80 Ω (800 Ω cm^{-2}) and 50 Ω (500 Ω cm^{-2}) for 15 and 20 wt.% CB, respectively. The effect of cycling is shown in Fig. 5 through impedance (Fig. 5(a)) and chronoamperometric plots (Fig. 5(b)). The low frequency capacitance, calculated from curves in Fig. 5(a) was found to vary little from 1 to 1.1 F but the serial resistance changed from 70 to 40 Ω and the medium frequency resistance (100 Hz) decreased from more than 50 to less than 30 Ω. Considering that the electrolyte resistance characterized at the highest frequencies (1 MHz) remained roughly constant, the resistance drop of the composite electrodes might be due to a geometrical relaxation of the material upon cycling. The limiting resistance of the current deduced from the chronoamperometric plots in Fig. 5(b) varied with cycling in a similar form from 65 to 30 Ω; however, the capacitance value was not directly extractable from the variation of the current since a deviation from the capacitive behaviour was quickly observed due to the diffusive contribution. Integrating the current from the last current plot (5000) a total charge of 1.4 C was calculated providing a discharge capacitance of 1.4 F (30% in excess of the impedance-
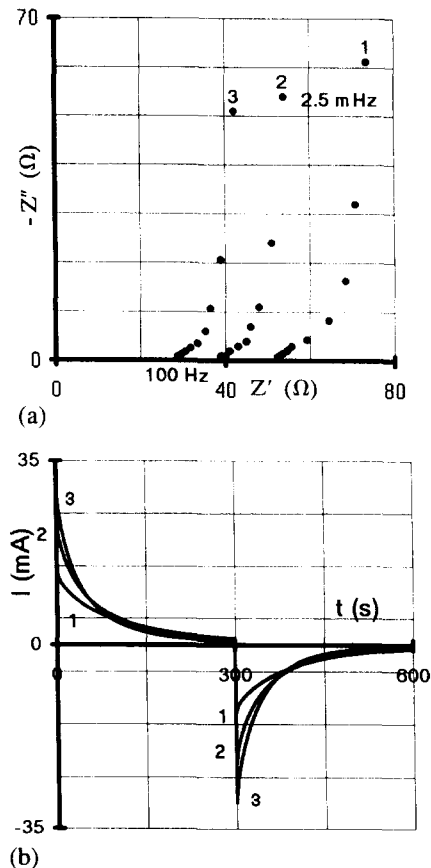

(a)

(b)

Fig. 5. Effect upon cycling of the complete cell (see Fig. 4 with 20 wt.% CB). (a) impedance plots; (b) chronoamperometric plots (pulse: 0 to 1 to 0 V). (1) first cycle; (2) after 1500 cycles, and (3) after 5000 cycles. (See conditions in Section 2.)

deduced capacitance). The discharge curves presented a perfectly symmetrical behaviour after charging between -2 and $+2$ V (Fig. 6). The leakage current was estimated at less than 1 μA cm^{-2} after a 3 h step potential of 0.5 V. Charging the cell (after 5000 cycles) with 2.5 mA cm^{-2} (chronopotentiometry), the potential reached 2 V in less than 90 s; the initial ohmic drop did indicate a resistance of 33 Ω and the initial linear variation a capacity of $\sim$1.1 F.

The cells showed a very good capability upon cycling up to at least 5000 cycles (more than 800 h of operation) which can be attributed to the high mechanical cohesion of the interfaces (porous surface of the collectors) and the good electrochemical stability of the electrolyte. Moreover, a substantial improvement of the electrical characteristics was observed. The pseudo-constant time of the cell (20 wt.% CB) was about 40 s, which means that 90% of the charge (2.5 C) was released in less than 90 s. The supercapacitor could store a maximum energy of 6.2 Wh l^{-1} (more than 20 kJ l^{-1}) and provided a peak power about 300 W l^{-1}. From these results a discharge capacitance value of 60 F g^{-1} of carbon (45

mg/electrode) was estimated which is significantly higher than for carbon-fibre cloth electrodes [5]. The device due to its thin-film constitution was completely flexible and could be handled with no apparent effect on the electrical properties.

Work is in progress to decrease the internal resistance of the devices and to better understand the complex electrochemical behaviour of the composite electrodes.
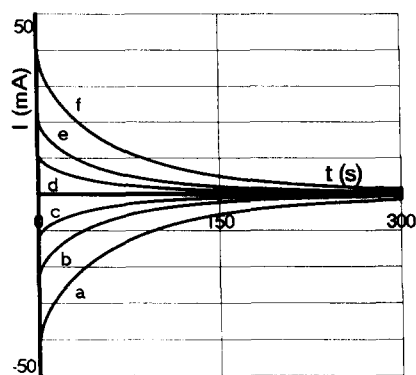
Acknowledgements

Fig. 6. Discharge curves current vs. time after charging of the cell for 10 min at: (a) -2 V; (b) -1 V; (c) -0.5 V; (d) $+0.5$ V; (e) $+1$ V, and (f) $+2$ V.

References

[1] B.E. Conway, J. Electrochem. Soc., 138 (1991) 1539.
[2] T. Tanaka, T. Susuki, K. Katsu, K. Okamoto and M. Hosokawa, NEC Res. Dev., 92 (1989) 57.
[3] (a) J. Sanada and M. Hosakawa, NEC Res. Dev., 55 (1979) 21; (b) I. Tanahashi, A. Yoshida and A. Atsushi, J. Electrochem. Soc., 137 (1990) 3052; (c) T. Kanbara, K. Nishimura, T. Yamamoto and K. Tokuda, J. Power sources, 32 (1990) 165; (d) I. Tanahashi, A. Yoshida and A. Nishino, Bull. Chem. Soc. Jpn., 63 (1990) 2029.
[4] I. Tanahashi, A. Yoshida and A. Nishino, Bull. Chem. Soc. Jpn., 63 (1990) 3611.
[5] (a) S. Sekido and Y. Ninimiya, Solid State Ionics, 3 (1986) 153; (b) Y. Matsuda, M. Morita, M. Ishikawa and M. Ihara, J. Electrochem. Soc., 140 (1993) L109.
[6] D. Barril, Thesis, Sherbrooke, Canada, 1991.
[7] P.G. Bruce, in J.R. MacCallum and C.A. Vincent (eds.), Polymer Electrolyte Reviews, Vol. 1, Elsevier Applied Science, Barking, UK, 1991, Ch. 8, p. 237.
[8] H. Kawamoto, in E.K. Sichel (ed.), Carbon Black–Polymer Composites, Marcel Dekker, New York, 1982, p. 135.