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Electrochemical properties of activated carbon supercapacitors prepared with solid state electrolytes based deep eutectic solvents

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1. Introduction

Current environmental problems and the need for efficient devices for capturing and storing energy have boosted research in this area, focused mainly on photovoltaic cells, batteries and double-layer electrical capacitors, currently known as electrochemical supercapacitors. The energy in the supercapacitor is stored through polarization followed by the migration of ionic charges on the surface of the electrodes. Due to the high surface area, porous structure and good conductivity, carbon-based electrodes are promising for application in supercapacitors. Traditional electrolytes are aqueous or organic, however electrolytes based on ionic liquids have also been used in electrochemical supercapacitors as they have a higher maximum operating potential (3.0 - 4.0 V), but may present some toxicity. An alternative class of ionic liquid is that of deep eutectic solvents (DES) which is based on a mixture of two compounds HBA and HBD (hydrogen bond acceptor and hydrogen bond donor). Eutectic solvents are compounds of natural origin such as: organic acids, amino acids, sugars, choline chloride and urea. Based on the individual properties of each component it is possible to state that they are considered non-toxic and biodegradable[1]. In this study, propylene glycol, glycerol, choline chloride, tetraethylammonium bromide and benzoic acid have been used as chemical starters reactants to DES preparation.

2. Methodology

Eutectic solvent-based supercapacitors with low environmental impact were prepared using commercial activated carbon electrodes with high surface area. The highly toxic organic electrolyte from these commercial electrodes was removed at low pressure (vacuum 10^{-2}mbar) at room temperature. Propylene glycol ($C_3H_8O_2$) and glycerol ($C_3H_8O_3$) were used as the liquid solvent for the quaternary salts[2]. The solid ionic reactants were choline chloride (ChCl), tetraethylammonium bromide ($(C_2H_5)_4NBr$) and also benzoic acid ($C_7H_6O_2$) were tested[3]. Also a mixture combining of lithium perchlorate ($LiClO_4$) and propylene glycol with glycerol ($C_3H_8O_3$) in proportions were also prepared for a comparison. Mixtures containing a liquid and a solid were prepared on a hot plate with magnetic stirring at 80ºC. The components based on two solids in various molar proportions were heated on a hot plate up to 120ºC so that the mixture was completely homogenized, also with magnetic stirring. The assembly of the electrochemical supercapacitors was carried out according to the standard procedure used in previous works[4]. The electrical properties of the supercapacitors were determined by cyclic voltammetry (Arbin BT-4 Analyzer with MITS-PRO software 4) at room temperature. The internal resistance was represented by the equivalent series resistance (ESR) and the equivalent parallel resistance (EPR).

3. Results and Discussion

Analyzes have been carried out employing a scan rate of 1 mVs^{-1} with potentials varying between 1.0 and 2.0 V for studying their influence on the specific capacitance. Figure 1 show the solid eutectic mixture of choline chloride and benzoic acid on the molar ratio (1:1). This was the best molar result for this combination of eutectic mixture for an electrochemical supercapacitor. The highest specific capacitance was found to be at a potential of 1.9 V (50±3 Fg^{-1}).

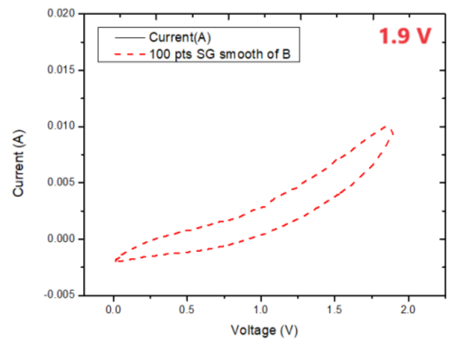

Figure 1: Cyclic voltammetry curve for the commercial carbon supercapacitor with electrolyte based on choline chloride with benzoic acid (1:1) at a sweep rate of 1 mVs^{-1} and at the potential 1.9 V.

To evaluate the behavior of electrolytes composed of lithium perchlorate and propylene glycol (1:1) and lithium perchlorate with glycerol (1:1) prepared in two distinct percentages. Best result was found at a potential of 2.0 V with a specific capacitance of 38±2 Fg^{-1} for the former, as shown in figure 2. At a potential of 1.3 V a specific capacitance of 33±2 Fg^{-1} was determined for the latter, as presented in figure 3.

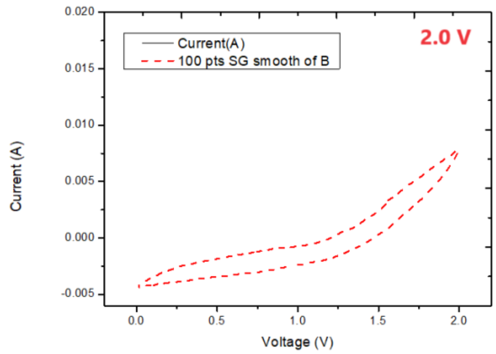

Figure 2: Lithium perchlorate plus propylene glycol (90%) mixed with lithium perchlorate plus glycerol (10%), both in (1:1) molar ratio measured at a potential of 2.0 V.

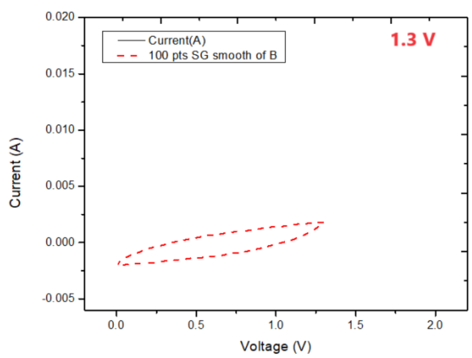

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Figure 3: Lithium perchlorate plus glycerol (1:1) measured at a potential of 1.3 V (0% of lithium perchlorate plus propylene glycol).

Combinations of eutectic solvents based on propylene glycol and tetraethylammonium bromide in a molar ratio of (1:1) yielded the highest specific capacitance result of 52±3 Fg^{-1} at a potential of 1.5 V, as depicted in figure 4. Analyzing the data collected on the different combinations of electrolytes it was possible to observe little modification on the specific capacitance values with a higher potential, but there is some deterioration the electrochemical supercapacitors. It is clearly noted that the most efficient electrolyte among all the investigated was the tetraethylammonium bromide with propylene glycol.

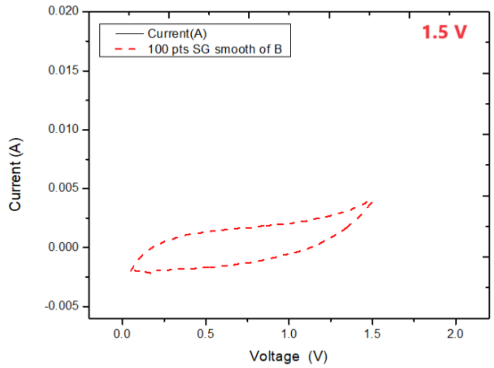

Figure 4: Eutectic solvents based on propylene glycol and tetraethylammonium bromide (1:1) with a potential of 1.5 V.

The ESR of the commercial supercapacitor in organic electrolyte at room temperature was evaluated using the galvanostatic cycle method and this is depicted in figure 5.

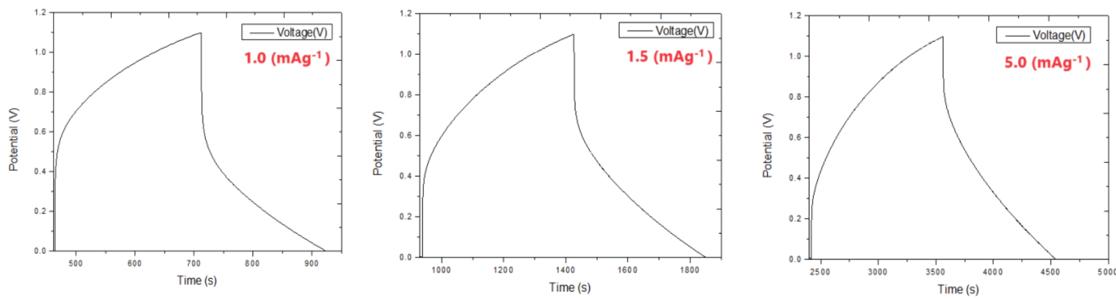

Figure 5: Charge and discharge curves obtained by the galvanostatic cycle for the electrolyte based on commercial organic electrolyte.

Current density (mAg^{-1})	ESR (Ω cm²)
1.0	105 ± 5
1.5	85 ± 5
5.0	80 ± 5

Table I: ESR values for commercial activated carbon supercapacitors with electrolyte based on the commercial organic electrolyte at a potential of 1.1 V.

4. Conclusions

Based on the results presented in this study it was possible to identify the most efficient solid electrolyte based on various deep eutectic solvents and this was the tetraethylammonium bromide with propylene glycol. The quaternary salt choline chloride mixed with benzoic acid solid electrolyte exhibited the lowest specific capacitance (27±2 Fg^{-1}). The electrolyte formed by lithium perchlorate and propylene glycol with addition of glycerol (10%) also showed reasonable capacitance (38±2 Fg^{-1}). Analysis of internal resistance of the supercapacitors using the galvanostatic cycle method showed that lower electrical current densities led to higher series resistance values.

Acknowledgements

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