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ELECTROLYTES FOR SUPERCAPACITORS BASED ON DIMETHYL SULFOXIDE AND TETRAALKYLAMMONIUM SALTS

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Solutions based on dimethyl sulfoxide (DMSO) and tetraalkylammonium salts were studied as electrolytes for supercapacitors. The specific conductivity and potential range of electrochemical stability for DMSO solutions were obtained, and galvanostatic studies of supercapacitors with these electrolytes were carried out.

Supercapacitors (or electrochemical double-layer capacitors, EDLCs) belong to the category of energy storage systems with high specific power and are widely used in industry (e.g. in hybrid electric vehicles, customer electronics, etc.) [1]. The operation principle of p supercapacitors is based on charging–discharging the electric double-layer by adsorption/desorption of electrolyte components on the surface and inside a porous electrode [2]. As electrolytes for EDLCs, aqueous, non-aqueous solutions and ionic liquids are used [3], and solutions of tetraalkylammonium (R_4N^+) salts in organic solvents are widely employed [1-5]. Their main benefit is a wide potential range at relatively high current densities providing hundreds thousands of charge/discharge cycles. A significant disadvantage of EDLCs is their low specific capacitance compared to the ‘classical’ energy storage devices, *i.e.* batteries.

Important factors defining the characteristics of a supercapacitor are the composition and properties of electrolyte solutions, namely their electrochemical window, thermal stability and conductivity. The widest class of electrolytes for EDLCs is presented by solutions based on acetonitrile, propylene carbonate, as well as other aprotic solvents and their mixtures [1–3]. Organic solvents employed in supercapacitors, methyl cyanide (s acetonitrile) on the first place, are far from being safe and pose environmental and health problems. This circumstance calls for the replacement of these solvents by environmentally friendly, non-toxic analogues, and dimethyl sulfoxide (DMSO) is a prospective candidate to satisfy such demands.

Electrolytes based on DMSO are not widely used in lithium batteries and supercapacitors. This is due to the structure features of DMSO, first of all, to the presence of S=O bond affecting interactions between the solvent and electrode materials. As a result of such interaction, the potential range of electrochemical stability is significantly reduced, and this is an issue for a number of composite electrode materials. The impact of adding DMSO on physico-chemical properties of electrolytes is described in Ref. [6]. It should be noted that characteristics of EDLCs with electrolytes based on DMSO and R_4N^+ salts are not presented in the literature. However, these electrolytes have a relatively low cost and allow for operating with a high concentration of the salt in their composition. Therefore, we aimed at filling this gap in the current work *via* a detailed study of DMSO-based solutions with various R_4N^+ salts as electrolytes for supercapacitors.

Experimental

In this study, tetraethylammonium tetrafluoroborate (Et_4NBF_4) and bis(oxalato)borate (Et_4NBOB), tetramethylammonium bis(oxalato)borate (Me_4NBOB), and bis(salicylato)borate (Me_4NBSB) were used. Me_4NBOB and Et_4NBOB were obtained by means of microwave synthesis according to Ref. [7].

Electrochemical measurements of carbon-based EDLCs with electrolytes were carried out in coin cells of 2016 type. All operations with electrolytes and cell assembling were performed in a glove box. The specific conductivity of solutions was determined from electrode impedance curves obtained by means of a Z-2000 impedancemeter (Elins, Russia) at the frequency range of 1–100 kHz. Measurements were carried out in the temperature range of -10–+70 °C in thermoplastic glass cells with flat parallel electrodes. A P-30 potentiostat (Elins, Russia) was used to determine the potential range of the electrochemical stability of electrolytes and to record cyclic voltammetric curves for EDLCs. Galvanostatic cycling for supercapacitor cells was performed by a TIONIT testing equipment (Ukraine).

Results and Discussion

Polytherms of the specific conductivity ($\ln k - 1/T$) for electrolytes with a concentration of 0.7 mol/kg of salts are presented in Fig. 1a. These dependences are almost the same for the Me_4NBOB , Et_4NBOB and Et_4NBF_4 , whereas the Me_4NBSB -based solution has significantly lower specific conductivity than other ones due to big differences in the size of bis(salicylato)borate, bis(oxalato)borate and tetrafluoroborate. A sharp decrease in the specific conductivity in the temperature range of 5...7 °C is caused by the freezing of solution, which can be observed

visually. The freezing point of the solution is ca. 10 °C lower than for pure DMSO (19 °C).

The polytherms of specific conductivity for the Me₄NBOB solutions with various salt concentrations (0.2 - 2.0 mol/kg) are linear in Arrhenius coordinates (Fig. 1b). The temperature of the liquid–solid transition decreases with increasing the salt concentration. For instance, such temperature for the solution of 0.2 mol/kg concentration is about 14 °C, that is 5 °C lower than for pure DMSO, while for the solution of 1.4 mol/kg concentration the temperature decrease is 18.5 °C.

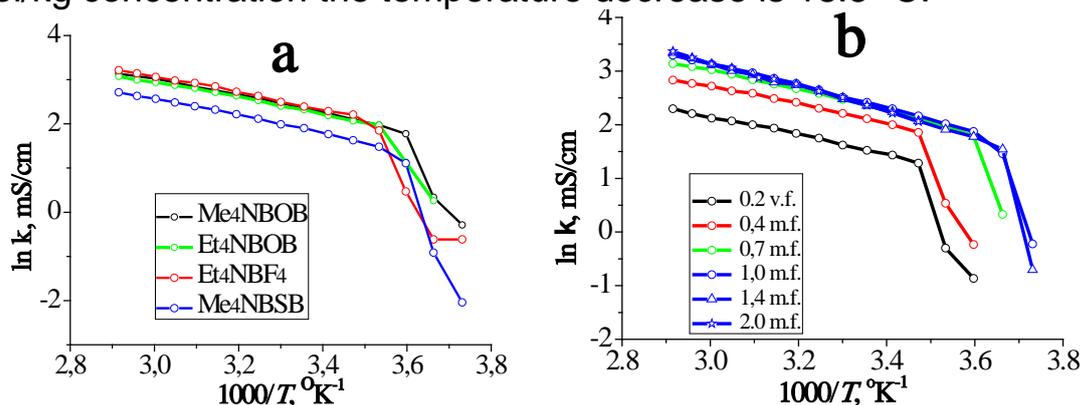


Figure 1. Polytherms of specific conductivity: (a) solutions containing 0.7 mol/kg of salts; (b) solutions of Me₄NBOB containing different salt concentrations

Fig. 2a shows cyclic voltammograms of Me₄N⁺-containing solutions in various aprotic solvents recorded on a platinum electrode. According to the data obtained the potential range of electrochemical stability is about 2.8–3.0 V for all electrolytes. Thus, it can be assumed that the voltage of the adsorption–desorption process will be of similar value. It is noteworthy that this potential range for acetonitrile and propylene carbonate solutions is nonsymmetrical and moves to the anodic region by nearly 500 mV unlike DMSO-based solutions, which have almost the same values of oxidation/reduction potentials.

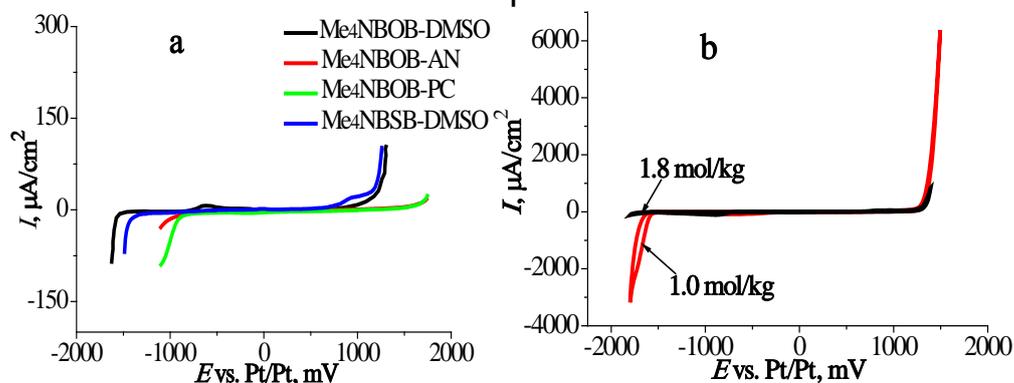


Figure 2. Cyclic voltammograms of (a) Me₄N⁺-containing solutions in various aprotic solvents of 0.7 mol/kg salt concentration and (b) Cyclic voltammograms of the Me₄NBOB–DMSO solutions of various salt concentrations. Pt electrode, 5 mV/s scan rate

As all DMSO-based electrolytes regardless of their cationic and anionic composition demonstrate a similar electrochemical behavior it may be suggested that this feature is determined by the properties of DMSO, namely its electrochemical stability in the anodic region. The increase of the salt concentration up to 1.8 mol/kg has a little effect on the width of the electrochemical window (Fig. 2b).

Galvanostatic charge–discharge curves registered at different voltages (from 0.9 V to 1.9 V) for EDLCs based on Me₄NBOB–DMSO and Et₄NBF₄–DMSO electrolytes with 0.7 mol/kg and 1 mol/kg salt concentration, respectively, are presented in Fig. 3. As in the case of voltammograms, increasing voltage above 1.5 V leads to the change of an almost ideal triangular view of the galvanostatic curves, while at higher voltages these curves are distorted due to faradaic processes.

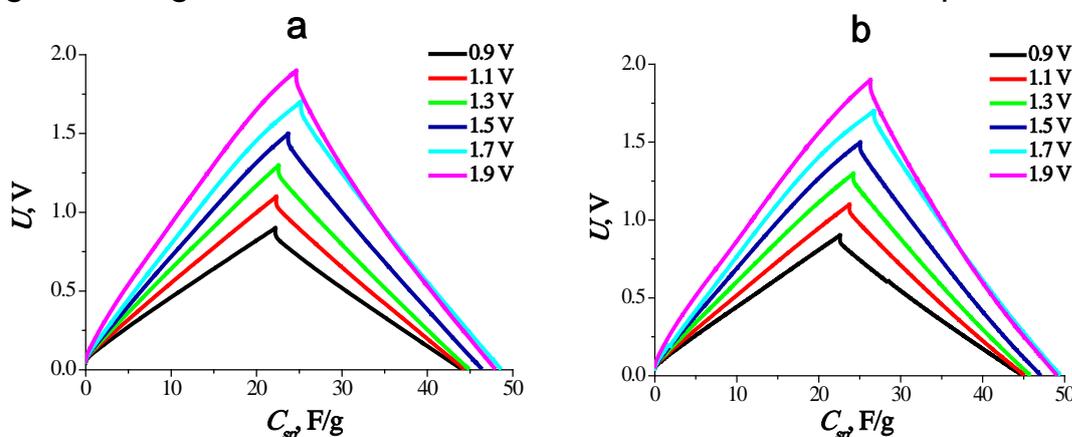


Figure 3. Galvanostatic charging–discharging curves for EDLCs at different cycling voltages: (a) 0.7 mol/kg Me₄NBOB–DMSO electrolyte; (b) 1.0 mol/kg Et₄NBF₄–DMSO electrolyte. 1 mA/cm² current density

A decrease in specific capacitance with the cycle number during galvanostatic charge–discharge to 1.9 V for EDLCs with Me₄BOB–DMSO and Et₄NBF₄–DMSO electrolytes is shown in Fig. 4. Increasing the cycling current leads to stabilization of the capacitance value.

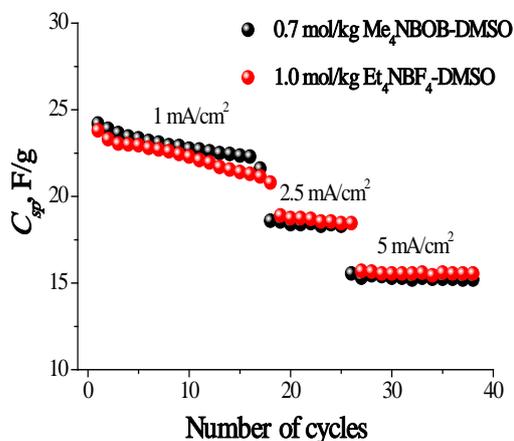


Figure 4. Dependences of specific capacitance for EDLCs with NoritDLC-Supra electrodes on cycle number and current density

Conclusions

The specific conductivity and potential range of electrochemical stability for DMSO of tetraalkylammonium salts solutions were obtained, and galvanostatic studies of supercapacitors with these electrolytes were carried out. Based on these data it could be concluded that DMSO based electrolytes might serve as an environmentally benign alternative to common acetonitrile solutions employed in commercial supercapacitors.

Acknowledgments

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