

# Cyclic Voltammetry and Electrochemical Impedance Studies of Electrolyte Characteristics on the Electrochemical Parameters of Supercapacitors

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Electrical double layer capacitors (EDLC), so-called supercapacitors based on two ideally polarizable nanoporous carbon electrodes (NPCE) (BET surface area  $\sim 1300 \text{ m}^2/\text{g}$ , prepared from TiC precursor by chlorination method) in propylene carbonate (PC) as the solvent for the 1 M  $\text{Me}_3\text{EtNBF}_4$ ,  $\text{Me}_2\text{Et}_2\text{NBF}_4$ ,  $\text{MeEt}_3\text{NBF}_4$ ,  $\text{Et}_4\text{NBF}_4$ ,  $\text{Et}_3\text{PrNBF}_4$  and  $\text{Et}_3\text{BuNBF}_4$  electrolytes have been tested by cyclic voltammetry and electrochemical impedance spectroscopy methods [1]. The cyclic voltammograms show that the ideal capacitor behaviour has been established at potential scan rates  $v \leq 10 \text{ mV s}^{-1}$  and  $\Delta E \leq 2.3 \text{ V}$  ( $\Delta E$  is so-called cell potential or voltage). Using the impedance data it was found, that the relaxation time constant  $t_R$ , obtained from the relaxation frequency  $f_R$ , is practically independent of  $\text{TAN}^+$  cation molar mass in the region of cell potential  $\Delta E \leq 2.0 \text{ V}$ . At  $\Delta E > 2.0 \text{ V}$ ,  $t_R$  somewhat increases in the order of salts  $\text{MeEt}_3\text{NBF}_4 \leq \text{Me}_2\text{Et}_2\text{NBF}_4 < \text{Et}_4\text{NBF}_4$ , i.e. with decreasing the molar conductivity of solution. At very low frequency  $f < 0.01 \text{ Hz}$ , the nearly equilibrium values of the series  $C_s$  and parallel  $C_p$  capacitances have been established for the nanoporous carbon electrode (NPCE) | PC +  $\text{TANBF}_4$  EDLC cells. However the coincidence of the  $C_s$  and  $C_p$  values at  $f < 0.005 \text{ Hz}$ , as well as the phase angle values  $\boldsymbol{d} \leq -75^\circ$  for NPCE | PC cells, to a first approximation, show that the adsorption equilibrium will be established only at very low frequencies [1,2].

The dependences of the normalized real  $P(\boldsymbol{w})/|S|$  and imaginary  $Q(\boldsymbol{w})/|S|$  parts of the complex power versus frequency and phase angle  $\boldsymbol{q}$  versus frequency dependences show that the relaxation time constant is independent of the  $\text{TAN}^+$  cation characteristics and the low frequency behaviour of the NPCE | PC +  $\text{TANBF}_4$  cell is mainly determined by the solvent characteristics [1,2].

Analysis of the experimental data for various systems shows that the Srinivasan and Weidner model [3] can be used to fit the Nyquist plots measured at fixed  $\Delta E$ . It was found that the effective conductivity for the electrolyte ions in the nanoporous matrix,  $\boldsymbol{k}$ , as well as the nanoporous carbon matrix conductivity,  $\boldsymbol{s}$ , increase with  $\Delta E$ . The increase of  $\boldsymbol{k}$  and  $\boldsymbol{s}$  with  $\Delta E$  can be explained by the migration of ions. Analysis of the impedance data indicates that the separator resistance  $R_s$  increases somewhat with decreasing the molar conductivity of the electrolyte used in the electrical double layer capacitors [1,2].

## References

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3. V. Srinivasan, J. Weidner, J. Electrochem. Soc. 146 (1999) 1650.