

Characterization of quaternary solvent mixture and Na-salt based electrolytes in a wide temperature range

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New electrolyte solutions and electrode materials, both for aqueous and non-aqueous supercapacitors (SCs), are being tested to develop devices having improved capacitance (electric double-layer or pseudocapacitance) and energy and power performance. Various possible SC applications require retaining high specific performance in a wide temperature range. Also the environmental effect of materials and solvents/salts used is of significant importance for large-scale application. Li-ion capacitors have been recently under focus to increase the cell voltage and capacitance of SCs by Li-predoping of negative carbon electrodes. As Na is a much more available and cheaper metal, there are also some studies on so-called Na-ion capacitors. Authors of this abstract have studied Li-salts and also Na-salts in a binary carbonate solvent system as electrolytes mainly for double-layer capacitive SCs at room-temperature [1,2]. In this study the focus is on the temperature dependence of electrochemical characteristics of Na-salts based SCs using a quaternary solvent mixture in the example of some previous works [3].

Electrochemical characteristics of 1 M electrolyte solutions of NaClO_4 , NaPF_6 and NaFSI (sodium bis(fluorosulfonyl)imide) in a quaternary solvent mixture were tested for application in SCs in a wide working temperature range (from -40 to 60 °C). The solvent mixture comprised of ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate (PC) and ethyl acetate (EA) in 1:1:1:0.5 ratio by volume. High surface area ($1680 \text{ m}^2 \text{ g}^{-1}$) carbide-derived carbon was used as electrode material. The SCs systems were assembled in hermetic aluminium test cells (Hohsen Corp.) in a glove-box. Detailed analysis of data from cyclic voltammetry, impedance spectroscopy and constant power charge/discharge (Ragone plots) methods was done for the systems under study.

The widest temperature range with the test system capacitance retained was established in case of NaPF_6 salt based system (Figure 1). Only at temperatures $T \leq -40$ °C decrease in capacitance, calculated from cyclic voltammograms, was observed. Faradaic decomposition of the NaPF_6 electrolyte starts at $T > 60$ °C and at cell potentials $\Delta E > 2.0$ V, however, the capacitance of the device is retained, and there is no quick blocking of the electrode surface by decomposition products. The calculated capacitance values from cyclic voltammetry curves (Figure 1) and impedance spectroscopy data (Figure 2) are in a good agreement. The NaClO_4 electrolyte based SC showed comparable or even slightly higher capacitance values at $T > 0$ °C, compared to NaPF_6 , but a quick decrease in capacitance was observed at lower temperatures (Figure 2). Extensive faradaic reactions were observed in case of NaFSI electrolyte based SCs already at $\Delta E > 2.5$ V, which is related to the oxidation of a thin aluminium current collector layer deposited onto the electrodes by magnetron sputtering, and also the aluminium test cell surface [4]. The addition of 0.1 M NaPF_6 to 0.9 M NaFSI did not have sufficient blocking (solid electrolyte interface formation) effect, i.e., there was no passivation of Al layer at higher cell potentials applied (Figure 2).

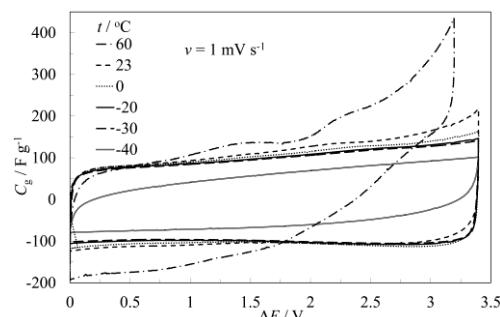


Figure 1. CVs presented as gravimetric capacitance C_g vs. cell potential ΔE for 1 M NaPF_6 in EC:DMC:PC:EA at different temperatures.

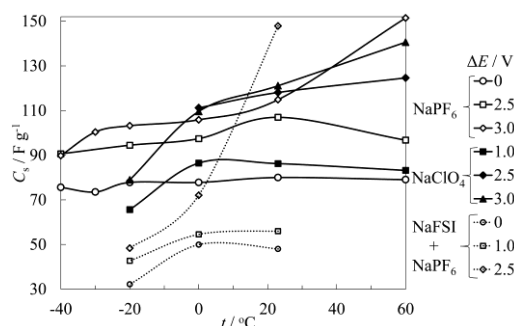


Figure 2. Series resistance C_s , calculated from impedance data, vs. temperature for different Na-salt solutions in EC:DMC:PC:EA at various cell potentials ΔE .

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