

Use of organic esters as co-solvents for electrical double layer capacitors with low temperature performance

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Abstract

The electrochemical characteristics of the electrical double layer capacitor (EDLC) single cell based on the nanoporous carbon electrode in 1 M $(\text{C}_2\text{H}_5)_3\text{CH}_2\text{NBF}_4$ (TEMA) solution in various non-aqueous organic carbonate and organic ester binary, ternary and quaternary solvent systems (ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), methyl formate (MF), methyl acetate (MA) and ethyl acetate (EA)) mixed in the x:y, x:y:z and x:y:z:f volume ratios, respectively) have been studied using the cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) methods. The specific capacitance, phase angle, series and parallel resistance values dependent on the solvent system used have been calculated. The region of ideal polarisability of nanoporous carbon electrodes $\Delta E \geq 3.0$ V for 1 M TEMA in various binary, ternary and quaternary non-aqueous solvent systems has been achieved. Specific conductivity values for 1 M TEMA solution in various organic carbonate – organic ester based electrolytes have been obtained at $-40^\circ\text{C} < T < 50^\circ\text{C}$ and compared with electrochemistry data.

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1. Introduction

The study and modelling of the electrochemical characteristics of the nanoporous materials as well as electrical double layer capacitors (EDLC-s) are very important problems taking into account the development of EDLC of high specific performances [1–15]. EDLC can supply high power during several seconds. High power density and very good cyclability make EDLC-s useful in the power electronic systems and very promising systems in many fields of technology: spatial, automotive, computer and etc. [1–15].

A very important problem is associated with the non-aqueous electrolyte properties [1,3–8] obtaining the characteristic relaxation frequencies, specific energy and power densities and other characteristics of EDLC-s, as the specific energy density depends on the region of ideal polariz-

ability of the interface between the nanoporous carbon electrode (NPCE) and non-aqueous electrolyte solution [16–18]. If the electrode material and electrolyte (i.e. salt) are stable in the polarisation region ΔE studied then the region of ideal polarizability is mainly obtained by the electrochemical stability of the solvent investigated.

The main aim of this paper is to study the influence of the new binary, ternary and quaternary solvent system characteristics, based on the organic carbonates (propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC)) and organic esters as co-solvents (ethyl acetate (EA), methyl acetate (MA) and methyl formate (MF)) on the nanoporous electrode/electrolyte interface characteristics. It should be noted that the binary and ternary as well quaternary solvent mixtures are widely studied as solvents for electrolytes for lithium ion batteries [19–22]. The liquid-solid phase diagrams of ternary and quaternary (quasiternary) organic carbonates calculated using the

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thermodynamics of non-ideal solution models for the carbonates in the liquid state were analysed by Ding [23].

In this work the electrochemical characteristics of EDLC have been obtained using the following solvent systems: EC:DMC, EC:EMC, EC:DEC, EC:EA, EC:MA, EC:MF, EC:DMC:EA, EC:EMC:EA, EC:DEC:EA, EC:DMC:MA, EC:DMC:MF, PC:DMC:EA and EC:DMC:DEC:EA in the various molar ratios. These systems have been selected because these solvents have different values of the relative macroscopic dielectrical permittivity (ϵ), different viscosity values and melting temperatures as well as different dipole moment values (vertical component) (μ) (Table 1). Additionally it should be mentioned that these solvents have very different solubility of salts and electrical conductivity at various temperatures (i.e. the electrolytes made have different molar conductivity values at given temperature). The replacement of acetonitrile (AN) with less harmful solvent or mixtures of solvents is a very important step for the wide commercialisation of EDLCs, because the AN is a toxic solvent and can not widely used for the production of EDLC for the consumer goods (electric cars, toys) and computer back-up systems, as well as various peak power generation systems. The addition of organic esters as co-solvents increases the solubility of tetraalkylammonium salts, decreases the viscosity of electrolyte and thus increase the specific conductivity of electrolyte in nanopores. The addition of organic ester into the organic carbonate electrolyte system decreases the series resistance of EDLC and therefore increases the energy density – power density values at fixed low temperature. The EDLC based on the organic carbonate or mixtures of various organic carbonates demonstrate the very low power densities at lower temperatures [1,4,10,13–18,24–29].

Table 1
Physical constants of dipolar organic solvents used for studies

Solvent	Dipole moment (μ/D)	Dielectric constant (25 °C) ϵ	Melting temperature (°C)	Molar volume (25 °C) $\text{dm}^3 \text{mol}^{-1}$
EC – ethylene carbonate	4.9	89	37	62
DMC – dimethyl carbonate	0.88	3.12	3	84
PC – propylene carbonate	4.94	64.92	–49	84
EMC – ethyl methyl carbonate	–	2.9	–55	104
DEC – diethyl carbonate	0.94	2.82	–43	122
MF – methyl formate	1.77	8.5	–99	62
MA – methyl acetate	1.72	6.68	–98	80
EA – ethyl acetate	1.82	6.0	–84	98
AN – acetonitrile	3.53	35.94	–49	53

2. Experimental

2.1. Supercapacitor cells and measurement systems

All the experiments discussed were made inside the glove box Labmaster 130 at very clean and dry conditions (O_2 and H_2O concentration lower than 1 ppm). The two-electrode cell was set in a hermetic aluminium test cell (Hohsen Corporation, Japan) to ensure the gas tightness of the cell. Between working electrodes the 25 μm thick Celgard 2400 separator sheet was used.

The pure argon (99.99995%, AGA) has been used for saturation of the anhydrous acetonitrile (AN), propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), ethyl acetate (EA), methyl acetate (MA) and methyl formate (MF) (“Merck”, Selectipur[®], moisture content by Karl Fischer titration method less than 30 ppm) and stored over molecular sieves before using for preparation of the 1 M $(\text{C}_2\text{H}_5)_3\text{CH}_3\text{NBF}_4$ (Stella Chemifa Corporation, Japan, assay $\geq 99.9\%$, moisture content < 100 ppm, additionally purified and tested [1–7]) electrolyte. Impedance spectra were recorded using a Solartron FRA 1255 and potentiostat 1286 over a frequency range $1 \times 10^3 \dots 1 \times 10^{-3}$ Hz, and 5 mV modulation was used.

2.2. Electrodes

The electrodes were constituted of the nanoporous carbon cloth AUVM (Ukraine), with the pore size distribution function given in Fig. 1, and specific surface area $\sim 1500 \text{ m}^2 \text{ g}^{-1}$ discussed in detail before [6–8,16–18], covered by the very pure Al layer from one side by the plasma activated physical vapour deposition method [6–8,16–18,24–29]. After that, the Al-covered carbon electrode was spot-welded in an Ar atmosphere to the Al-foil current collector. The limits of ideal polarizability of Al foil have been established by cyclic voltammetry as well as by impedance spectroscopy methods, and are wider than those for carbon cloth electrode used. Before assembling the working electrode, the carbon cloth material was heated at $T = 300$ °C during 48 h under reduced pressure ($p < 10^{-3}$ atm). The electrode area used was 2 cm^2 and medium thickness $\sim 300 \mu\text{m}$.

2.3. Gas phase characteristics of electrode material

Specific surface area, pore size distribution, micropore volume, micropore area and other parameters were measured using the Gemini Sorptometer 2375 (Micromeritics Inc.) system and calculated according to the methods discussed in [30]. Some more important characteristics obtained are given in Table 2 and Fig. 1. According to the data in Fig. 1, the nanopores with a pore diameter $d_1 = 1.4 \text{ nm}$ as well as wider pores $d_2 \geq 2.0 \text{ nm}$ prevail on the surface of carbon. The specific area of nanoporous carbon, obtained by the Brunauer, Emmett and Teller (BET)

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