

## Fluoroethylene Carbonate and Propylene Carbonate Mixtures Based Electrolytes for Supercapacitors

A. Jänes, T. Thomberg, J. Eskusson, E. Lust  
Institute of Chemistry, University of Tartu,  
14a Ravila Str., 50411 Tartu, Estonia

The main aim of this paper is to study the influence of the binary solvent system characteristics, based on the propylene carbonate (PC, 4-methyl-1,3-dioxolan-2-one) and fluoroethylene carbonate (FEC, 4-fluoro-1,3-dioxolan-2-one) on the microporous TiC-CDC electrode|electrolyte interface characteristics [1]. It should be mentioned that FEC is used as an excellent additive or solvent for the secondary lithium ion batteries. FEC suppresses the decomposition of the electrolyte solution and increases the efficiency of the charge and discharge processes of lithium ion batteries. Partial fluorination of organic solvents often increases their polarity, and the use of the fluorinated solvent, improves the performance of lithium ion batteries. The freezing point of PC and FEC are  $-54.53\text{ }^{\circ}\text{C}$  and  $17.3\text{ }^{\circ}\text{C}$ , respectively. The monofluorination of dimethyl carbonate and ethylmethyl carbonate increases relative permittivity, dynamic and kinematic viscosities. The dynamic viscosity of FEC (4.1 mPa s at  $40\text{ }^{\circ}\text{C}$ ) is higher than that for PC (2.53 mPa s at  $25\text{ }^{\circ}\text{C}$ ), and the relative permittivity of FEC (78.4 at  $40\text{ }^{\circ}\text{C}$ ) is higher than that of PC (64.92 at  $25\text{ }^{\circ}\text{C}$ ). The replacement of acetonitrile (AN) with less harmful and less flammable solvent or mixtures of solvents is a very important step for the wide commercialization of SCs, because the AN is a toxic solvent and cannot widely used for the production of SC for the consumer goods and computer back-up systems, as well as of various peak power generation systems [2-5].

In this work the dynamic viscosities of FEC, PC and FEC:PC mixtures (vol. %) were measured at fixed temperatures from  $-20$  to  $60\text{ }^{\circ}\text{C}$  using U-shaped viscosimeter with flow pipe diameter 0.82 mm. The dynamic viscosity somewhat increases with the rise of FEC vol.% in mixed solvent system, especially at lower temperatures  $T < 0\text{ }^{\circ}\text{C}$ . The electrochemical characteristics of supercapacitors (SCs) have been obtained using the following solvents and solvent systems: PC, FEC, and mixtures of FEC:PC in various volume ratios: 1:1 (50 vol.% FEC), 1:9 (10 vol.% FEC) and 1:19 (5 vol.% FEC) [1]. These systems have been selected because mentioned solvents have different relative macroscopic dielectrical permittivity, viscosity values, and melting temperatures as well as different dipole moment (vertical component) values.

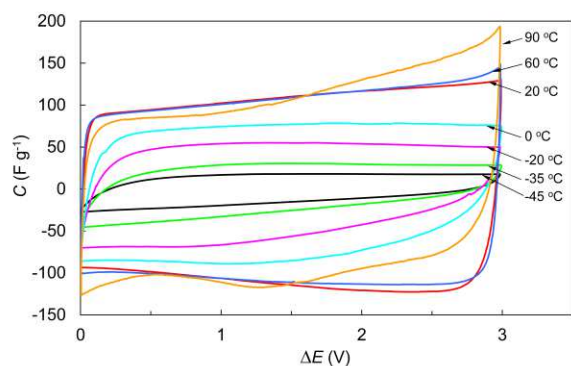


Fig. 1. Cyclic voltammograms expressed as capacitance vs. cell potential curves for FEC:PC (1:19) with addition of  $1\text{ M } (\text{C}_2\text{H}_5)_3\text{CH}_3\text{NBF}_4$  at scan rate  $10\text{ mV s}^{-1}$  and at different temperatures.

The rectangular shape of the cyclic voltammograms expressed as capacitance vs. cell potential ( $C, \Delta E$ ) show that the so-called nearly ideal capacitor behaviour has been established at cell potential scan rates  $v \leq 10\text{ mV s}^{-1}$  and  $\Delta E \leq 3.0\text{ V}$  even at  $T \leq -35\text{ }^{\circ}\text{C}$  (Fig. 1). The potential scan rate at which the deviation of cyclic voltammograms from the rectangular shape can be seen in the region of potential switch over decreases with the decrease of density of electrolyte. Thus, the dependence of the shape of the current — cell potential curves on the solvent system used is mainly influenced by the increase of the series resistance of electrolyte caused by the noticeably higher viscosity and lower molar conductivity of PC, FEC, FEC:PC (1:1) and FEC:PC (1:9) compared with FEC:PC (1:19) based electrolyte at lower  $T \leq -35\text{ }^{\circ}\text{C}$ .

Similarly to the other non-aqueous electrolyte systems, noticeable increase of  $C_s$  (Fig. 2a) at  $f < 1.0\text{ Hz}$  takes place, and at  $f \leq 5 \times 10^{-3}\text{ Hz}$ , plateaus in  $C_s$ ,  $\log f$  plots have been established. Low frequency ( $C_s (\omega \rightarrow 0)$ ) values increase from FEC to FEC:PC (1:19) mixed solvent based system. For FEC:PC (1:19) nearly 2 times higher values of  $C_s (\omega \rightarrow 0)$  have been calculated. The  $C_s$  values depend very strongly on temperature applied, however, for FEC:PC (1:19) based system, less pronounced dependence of  $C_s$  on  $T$  has been observed (Fig. 2b).

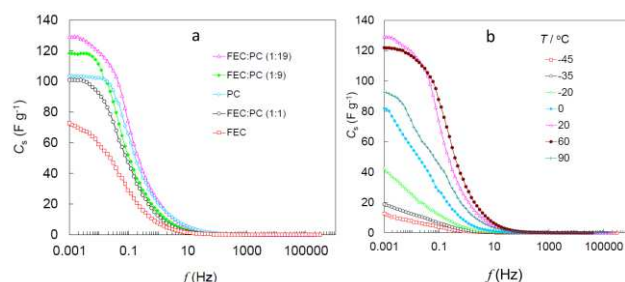


Fig. 2.  $C_s$  vs. ac frequency plots ( $\Delta E = 3.0\text{ V}$ ) for the EDLCs, based on different solvent systems, at  $T = 20\text{ }^{\circ}\text{C}$  (a) and for FEC:PC (1:19), at different temperatures (b), with addition of  $1\text{ M } (\text{C}_2\text{H}_5)_3\text{CH}_3\text{NBF}_4$ .

### References

1. A. Jänes, T. Thomberg, J. Eskusson and E. Lust, *J. Electrochem. Soc.*, **160**, A1025 (2013).
2. A. Jänes, L. Permann, M. Arulepp and E. Lust, *Electrochem. Commun.*, **6**, 313 (2004).
3. E. Lust, A. Jänes and M. Arulepp, *J. Electroanal. Chem.*, **562**, 33 (2004).
4. A. Jänes, L. Permann, M. Arulepp and E. Lust, *J. Electroanal. Chem.*, **569**, 257 (2004).
5. A. Jänes and E. Lust, *J. Electroanal. Chem.*, **588**, 285 (2006).