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**Toetab TÜ ja TTÜ doktorikool  
“Funktsionaalsed materjalid ja tehnoloogiad” (FMTDK)**

**ESF projekt 1.2.0401.09-0079**

# ELECTROCHEMICAL BEHAVIOUR OF CARBIDE DERIVED CARBONS IN $\text{LiPF}_6$ AND $\text{LiCF}_3\text{SO}_3$ NON-AQUEOUS ELECTROLYTES

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Electrochemical double layer capacitors (EDLC) have received much attention over the last decade due to their possible application as high-power density pulse generation and energy storage devices [1]. The replacement of acetonitrile (AN) with less harmful and flammable mixtures of solvents is a very important step for the wide commercialization of EDLCs.

A very important problem is associated with the non-aqueous electrolyte (salt) properties obtaining the specific energy and power densities and other characteristics of EDLC. It is very well established that the specific energy density depends mainly on the specific capacitance as well as potential region of ideal polarizability of the interface between the porous carbon electrode and non-aqueous electrolyte solution [2,3]. Overvoltage for electroreduction and electrooxidation of complex cations as well as anions is a very basic parameter obtaining the region of ideal polarizability of carbon | electrolyte interface.

Two- and three-electrode set-ups have been completed [4]. Li-ring electrode was used as a reference electrode and a counter electrode prepared from carbide derived carbon nanopowder with very large surface area has been used. The working electrode was either a graphitized vanadium carbide derived carbon C(V) or a microporous titanium carbide derived high surface area carbon C(TiC). 1 M  $\text{LiCF}_3\text{SO}_3$  in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1) mixture was used as electrolyte and the results were compared with similar electrode systems using 1 M  $\text{LiPF}_6$  in the same mixture of solvents.

There is a noticeable dependence of limiting capacitance obtained from cyclic voltammetry on the electrolyte salt studied. For two-electrode system solid electrolyte interface (SEI) formation takes place at  $E \leq 0.5$  V (vs.  $\text{Li}/\text{Li}^+$  reference electrode).

The Nyquist plots (Fig.1) show that the processes on the C(TiC) electrode | 1 M  $\text{LiCF}_3\text{SO}_3$  + EC/DMC interface are mixed kinetic limited and the adsorption and mass transfer processes both are rate limiting steps, different from 1 M  $\text{LiPF}_6$  electrolyte that demonstrates nearly ideal polarisability (Fig.2). The three-electrode measurements show that C(V)  $S_{\text{BET}} = 236 \text{ m}^2 \text{ g}^{-1}$  has almost two times smaller capacitance compared to C(TiC)  $S_{\text{BET}} = 1698 \text{ m}^2 \text{ g}^{-1}$ , which is due to its smaller surface area and the absence or negligible extent of the expected lithium intercalation. The systems with 1 M  $\text{LiPF}_6$  give much higher capacitance at negatively charged surface compared with 1 M  $\text{LiCF}_3\text{SO}_3$  and sharp

pseudocapacitive peaks at positively charged surface, which suggests that  $\text{PF}_6^-$  adsorption is stronger than  $\text{Li}^+$ . Based on impedance measurements mixed kinetic processes prevail on the surface of electrodes studied.

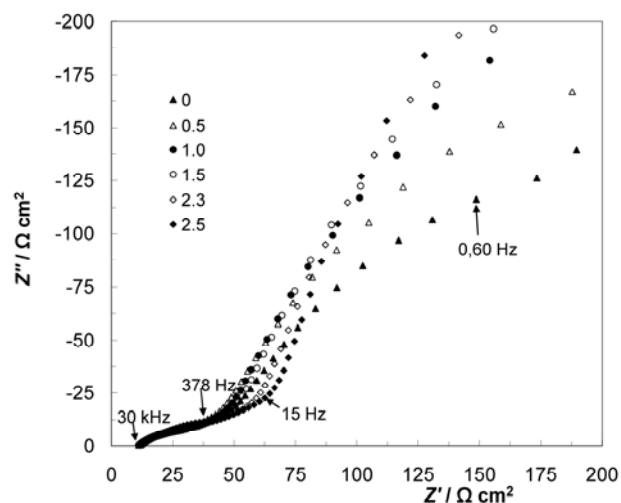


Fig.1. Impedance spectra of two-electrode C(TiC) | 1 M  $\text{LiCF}_3\text{SO}_3$  + EC/DMC system.

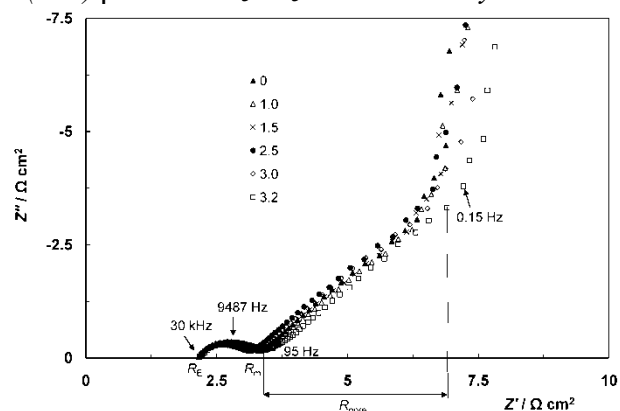


Fig.2. Impedance spectra of two-electrode C(TiC) | 1 M  $\text{LiPF}_6$  + EC/DMC system.

## References

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