

Surface analysis of supercapacitor electrodes after long-lasting constant current tests

Alar Jänes, Jaanus Eskusson and Enn Lust

Institute of Chemistry, University of Tartu, 14 a Ravila Str., 50411, Tartu, Estonia

E-mail: alar.janes@ut.ee

Abstract. FIB-SEM, XPS, TOF-SIMS and electrochemical methods have been used for the characterisation of physical properties and chemical composition of microporous carbide derived carbon electrodes, prepared from TiC at 950 °C (noted as TiC-CDC) after 40000 charge/discharge cycles. Changes in surface chemical composition of TiC-CDC electrodes, includes partial contamination with reaction intermediates (F_2 , CHO^+ , CN^+ , organic radicals), and Al current collectors, like partial dissolution of Al from positively charged electrode and deposition of Al onto the negatively charged TiC-CDC electrode surface, have been analysed.

1. Introduction

Mainly two types of electrochemical energy storage devices are available: supercapacitors (SC) and batteries. Supercapacitors (also called electrochemical capacitors), as energy storage devices with high power density and long cycle life, but moderate energy density, are considered as a promising high power density electrochemical energy sources in combination with batteries for hybrid electrical vehicles, combined solar cells and wind power systems etc., i.e., for development of combined energy recuperation complexes [1]. For the long-lasting exploitation and optimal specific energy — specific power regime, in addition to the optimized micro- and mesoporous structure of carbon material, the long-lasting electrochemical time stability of electrode material, electrical contacts and electrolyte is extremely important [2-5].

This paper reports the results of investigations of the electrochemical behaviour and surface chemical composition of the supercapacitor electrodes based on Al current collectors and deposited Al layers on microporous carbon TiC-CDC, prepared from TiC (Alfa Aesar, 99.5%, 2 μm powder) at $T_{synt} = 950$ °C and 1.5 M $(C_2H_5)_3CH_3NBF_4$ in acetonitrile (AN) as an electrolyte. Based on the N_2 sorption data, the multipoint BET surface area $S_{BET} = 1698$ m² g⁻¹ and micropore area (obtained using *t-plot* method) $S_{micro} = 1661$ m² g⁻¹ were calculated. Our previous SC studies indicate that TiC-CDC is an excellent supercapacitor electrode material containing micropores for adsorption of partially desolvated ions and a small quantity of mesopores for quick mass transfer of ions inside the porous TiC-CDC. However, from data available in literature it was recognized that, more detailed studies discussing the electrochemical behavior of Al-contact layers, deposited onto TiC-CDC carbon electrodes and Al current collectors at cell voltages $U \geq 3.2$ V, are inevitable [6-8].

2. Experimental

Before long-lasting electrochemical constant current charge/discharge (CC/CD) tests of SC the crystallinity and structure of the TiC-CDC electrodes were evaluated by focused ion beam scanning



electron microscopy (FIB-SEM) and X-ray photoelectron spectroscopy (XPS) with a Cu anode to generate CuK α radiation ($\lambda=1.5406$ Å). The Raman spectra were recorded using a Renishaw micro-Raman spectrometer equipped with 50 \times objective and 488 nm Ar⁺ ion laser with maximum radiation power of 15 mW on the sample. XRD and Raman data show that TiC-CDC carbon has mainly amorphous structure. The FIB-SEM data have been obtained using HeliosTM Nanolab 600. The XPS experiments were carried out with a SCIEHTA SES-100 spectrometer by using an unmonochromated MgK α X-ray source with power of 300 W. SES-100 spectrometer was calibrated using Au 4f photolines. The pressure in the analysis chamber was varied within the range from 2×10^{-10} to 5×10^{-10} mbar. Time of flight secondary ion mass spectrometry (TOF-SIMS) spectra were measured using PHI TRIFT V *nanoTOF* surface analysis instrument (Physical Electronics, Inc., USA) with a 30 keV Au⁺ ion gun. The acquisition time was 2.75 min and the TOF-SIMS spectra were collected in the range from 1 to 150 m/z in both the positive and negative polarities.

The SC electrode active material was prepared from TiC-CDC with 4 wt% addition of the binder polytetrafluoroethylene mixture (PTFE, 60 % solution in H₂O). The mixture received was laminated and roll-pressed to form a flexible layer of an active electrode material with thickness 100 ± 5 μ m. The Al current collectors were deposited onto the one side of a TiC-CDC electrode using the plasma activated physical deposition method. Thereafter the two-electrode standard aluminium test cell with two identical electrodes (apparent area of ~ 1.53 cm²) was completed and all electrochemical experiments were carried out at temperature 20 ± 1 °C. 25 μ m thick TF4425 sheet was used for mechanical separation of the working TiC-CDC electrodes from each other and 1.5 M (C₂H₅)₃CH₃NBF₄ solution in acetonitrile (AN) was used as an electrolyte [2-14].

3. FIB-SEM, XPS and TOF-SIMS analysis

FIB-SEM combined energy dispersive X-ray (EDX) method was used for the quantitative analysis of the SC electrodes. It was found that before electrochemical tests the porous TiC-CDC electrodes consist of particles with variable linear dimension from 1 to 3 μ m. Some oxygen has been observed on both TiC-CDC layers and Al current collectors being higher at Al containing ingredients. After 40000 charge/discharge cycles from 0.2 to 3.4 V the supercapacitor cells were opened and electrodes were washed and tried under vacuum. Thereafter TiC-CDC electrodes and Al current collectors were analyzed again by using XPS and FIB-SEM-EDX methods. Based on the analysis of data some changes in chemical composition of TiC-CDC electrode surface layers and Al current collectors have been detected after cycling. Weight % of TiC-CDC on carbon electrode was somewhat lower for negatively charged electrode (from 63 to 83 wt%) compared with that for positively charged electrode (from 87 to 92 wt%) or for the electrochemical untreated electrode. Noticeable increase of fluorine wt% for negatively charged electrode was detected, which is caused by the irreversible electroreduction of BF₄⁻ anions and adsorption of reaction intermediates or products (BF₃ and/or F₂) inside microporous TiC-CDC. Weak increase of N and O wt% at negatively charged electrode has been established caused by adsorption/absorption of (C₂H₅)₃CH₃N⁺ and O₂ decomposition products (hydrogen peroxide) during complex electroreduction reactions. Differently from negatively charged TiC-CDC, only very small increase in N and O wt% has been established for positively charged TiC-CDC electrode.

After 40000 electrochemical charge/discharge cycles an increased amount of N as well as F wt% on Al-coated side of TiC-CDC was observed, being higher for negatively charged electrode. According to EDX data the oxygen amount at Al contacts for both electrodes was quite low (7-10 wt%) which indicates, that the irreversible oxidation of aluminium during long-lasting cycling at high cell voltage was very slow.

The XPS analysis (Fig. 1) shows that the intensity of XPS peaks is somewhat different for TiC-CDC electrodes before and after long-lasting constant current charging/discharging tests. The O(KLL, (Auger lines)), O1s and N1s peaks for positively and negatively charged TiC-CDC electrodes are more pronounced than for the electrochemically non-tested electrode indicating to the peroxide

formation (negatively charged electrode) and OH^- adsorption/absorption (positively charged electrode) in microporous carbon have taken place.

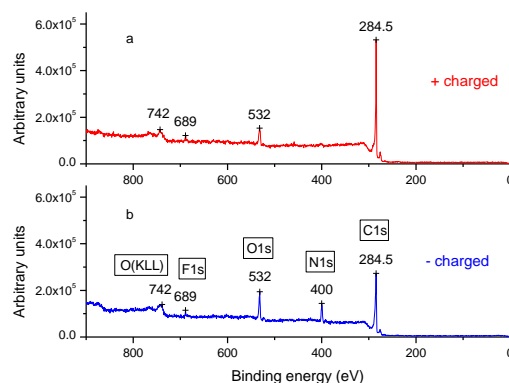


Fig.1. XPS spectra for positively (a) and negatively (b) charged electrodes after 40000 charge/discharge cycles.

Comparison of C1s peaks shows that after CC/CD tests the intensity of C1s peak is highest for positively charged TiC-CDC electrode, indicating to the formation of C-H bonds. However, this peak can be related to the modification of TiC-CDC surface as well as to the recrystallization of carbon particles from amorphous to more stable graphite like structure (so-called carbon electrode corrosion widely discussed in the case of H_2O medium). However, the intensity of F1s peaks is nearly independent of electrochemical testing time (i.e. polarization applied) indicating that there is no big degradation of Teflon binder under CC/CD cycling conditions. Existence of N1s peak in XPS spectrum indicates to the chemisorption of $(\text{C}_2\text{H}_5)_3\text{CH}_3\text{N}^+$ cations disproportionation products at negatively charge TiC-CDC electrode.

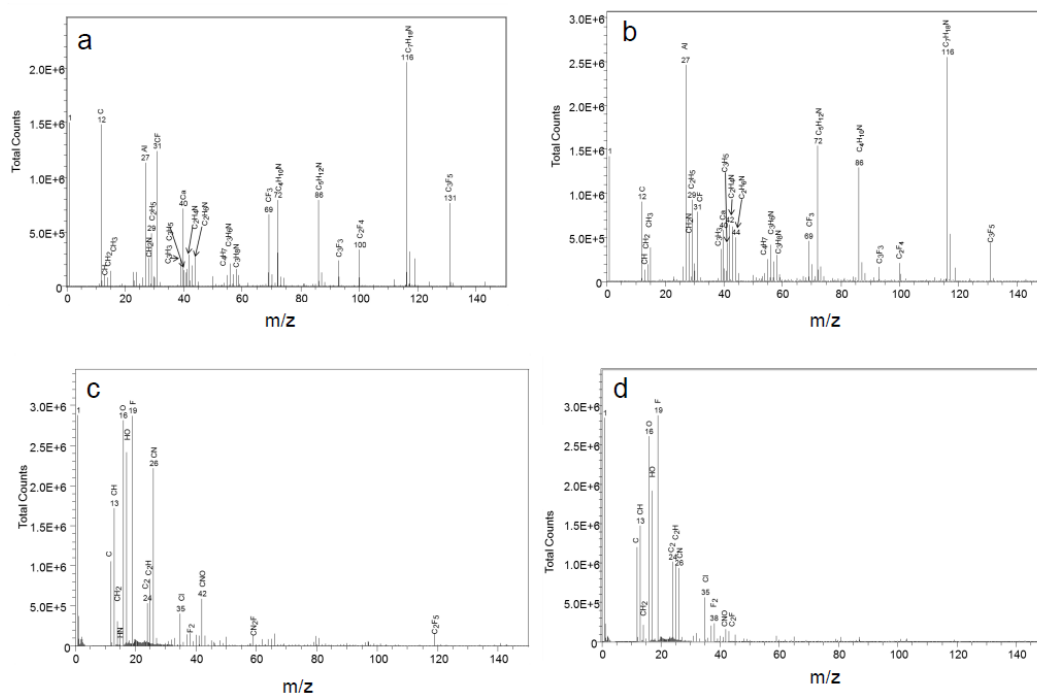


Fig.2. TOF-SIMS spectra for TiC-CDC supercapacitor for positively (a, c) and negatively (b, d) charged electrodes and for negatively (c, d) and positively (a, b) charged secondary ions after 40000 charge/discharge cycles.

After 40000 galvanostatic cycles from 0.2 to 3.4 V the supercapacitor electrodes were investigated by TOF-SIMS method up to ion masses $m/z = 150$. The mass spectra given in Figs. 2a – 2d demonstrate that the results for negatively and positively charged secondary ions obtained for positively and negatively charged electrodes are somewhat different. Mass spectrum for positively charged secondary ions shows mainly fragments or deposits formed from $(C_2H_5)_3CH_3N^+$ cations (13, 14, 15 m/z and 29 m/z for CH^+ , CH_2^+ , CH_3^+ and $C_2H_5^+$, respectively). Mass spectrum for negative charged secondary ions shows existence of CH^- (13 m/z), F^- (19 m/z), OH^- (17 m/z), CNO^- (42 m/z), O^- (16 m/z) and toxic CN^- (26 m/z) and other negatively charged fragments that are formed during $(C_2H_5)_3CH_3NBF_4$ and acetonitrile disproportionation and carbon electrode degradation processes. The positive characteristic fragment for PTFE ions and their nominal mass-to-charge ratios are: CF^+ (31 m/z), CF_3^+ (69 m/z), $C_3F_3^+$ (93 m/z), $C_2F_4^+$ (100 m/z), $C_3F_5^+$ (119 m/z) and $C_3F_5^+$ (131 m/z). In the negatively charged ion spectrum, the characteristic peaks of PTFE include $C_2F_5^-$ (119 m/z). In addition to the contaminants generated by electrochemically induced oxidation/reduction processes, common contaminants such as Na^+ (23 m/z), K^+ (39 m/z), Ca^+ (40 m/z) and adventitious hydrocarbons in the positive ion spectra and Cl^- (from synthesis of $(C_2H_5)_3CH_3NBF_4$ salt) were observed.

4. Conclusions

FIB-SEM, XPS and TOF-SIMS methods have been used for the chemical analysis of supercapacitor electrodes prepared from microporous carbide derived carbon synthesised from TiC at 950 °C, noted as TiC-CDC. The FIB-SEM, XPS and TOF-SIMS data show that partial contamination of carbon electrode surfaces with reaction intermediates (F_2 , CH^- , CHO^- , CN^- , organic radicals etc.) is a reality during galvanostatic charging and discharging. Al redeposition onto negatively charged carbon and restructuring of carbon particles was observed for positively charged TiC-CDC electrode.

Acknowledgements

This work was supported by the Estonian Science Foundation under Projects Nos. 8172 and 9184, Estonian Ministry of Education and Research project SF0180002s08 and European Regional Development Fund Project SLOKT10209T, Estonian Centres of Excellence in Research Project TK117T "High-technology Materials for Sustainable Development". Dr. L. Matisen and Dr. A. Kikas (Institute of Physics, University of Tartu) are thanked for the help with the XPS measurements. Dr. G.L. Fisher from Physical Electronics, Inc. (Chanhassen, MN, USA) is thanked for the assistance of TOF-SIMS measurements.

References

- [1] Conway B E 1999 *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications* (Kluwer Academic/Plenum Publishers, New York)
- [2] Jänes A, Eskusson J, Kanarbik R, Saar A and Lust E 2012 *J. Electrochem. Soc.* **159** A1141
- [3] Tallo I, Thomberg T, Kontturi K, Jänes A and Lust E 2011 *Carbon* **49** 4427
- [4] Jänes A, Thomberg T and Lust E 2007 *Carbon* **45** 2717
- [5] Eskusson J, Jänes A, Kikas A, Matisen L and Lust E 2011 *J Power Sources* **196** 4109
- [6] Laheäär A, Jänes A and Lust E 2011 *Electrochim. Acta* **56** 9048
- [7] Laheäär A, Jänes A and Lust E 2012 *Electrochim. Acta* **82** 309
- [8] Jänes A, Permann L, Arulepp M and Lust E 2004 *J. Electroanal. Chem.* **569** 257
- [9] Jänes A, Kurig H, Romann T and Lust E 2010 *Electrochem. Commun.* **12** 535
- [10] Jänes A, Permann L, Nigu P and Lust E 2004 *Surf.Sci.* **560** 145
- [11] Thomberg T, Jänes A and Lust E 2009 *J. Electroanal. Chem.* **630** 55
- [12] Thomberg T, Jänes A and Lust E 2010 *Electrochim. Acta* **55** 3138
- [13] Laheäär A, Kurig H, Jänes A and Lust E 2009 *Electrochim. Acta* **54** 4587
- [14] Palm R, Kurig H, Tõnurist K, Jänes A and Lust E 2012 *Electrochim. Acta* **85** 139