Increasing the stability of very high potential electrical double layer capacitors by operando passivation

M. Pohl, I. Tallo, A. Jänes*, T. Romann, E. Lust
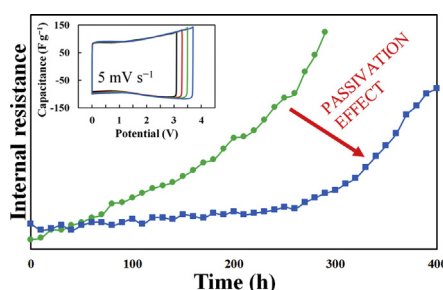
Institute of Chemistry, University of Tartu, 14A Ravila Str., 50411 Tartu, Estonia

HIGHLIGHTS

- Decrease of faradic reaction currents at higher potentials has been achieved.
- Nearly ideal capacitive behaviour ($\Delta E \leq 3.7$ V) after electrode surface passivation.
- Energy density higher than 30 Wh kg^{-1} at high power densities 40 kW kg^{-1}.

GRAPHICAL ABSTRACT

ARTICLE INFO

Keywords:
Carbide-derived carbon
Supercapacitor
Acetonitrile
Passivation
Overpotential
High power density

ABSTRACT

Electrochemical behaviour of titanium carbide-derived carbon (TiC-CDC) electrodes in 1 M $(C_2H_5)_3CH_3NBF_4$ + acetonitrile electrolyte has been studied using cyclic voltammetry, constant current charge-discharge, impedance and constant power methods. After step by step cell potential widening and repetitive cell potential cyclization up to 3.4 V, surface passivation, i.e. decrease of faradic reaction currents at potentials higher than 3.4 V, has been detected. Based on Raman spectroscopy data, the passivation effect has been explained by repetitive oxidation-reduction of more active carbon sites from the surface of TiC-CDC and exposition of the more stable graphitic regions. After very careful electrode surface passivation/modification, the region of ideal polarizability can be widened up to 3.7 V and nearly ideal capacitive behaviour with phase angle more negative than −88° and stable series capacitance (~120 F g^{-1}) have been obtained. Very high experimental energy densities (30 Wh kg^{-1}) at power densities 40 kW kg^{-1} ($\Delta E \geq 3.4$ V) have been measured, comparable even with the sol-gel TiC-CDC/(acetonitrile + $(C_2H_5)_3CH_3NBF_4$) two-electrode electrical double layer capacitor system. Much higher energy and power values have been achieved at $\Delta E = 3.7$ V, being the maximal cell potential limit, where nearly ideal polarizability for few hundred cycles was achieved.

1. Introduction

Modern society needs vast quantities of versatile energy storage for smooth and effective functioning [1–17]. Environmental contamination of some regions and growth of megacities has additionally increased the necessity for new energy storage devices with high power and energy densities needful for the stable integration of sustainable, but fluctuating photovoltaic, wind and concentrated solar power generation systems into large-scale electricity grids. With rapid growth of portable electronic applications, high performance miniature electrical energy storage devices are also needed [8–11,14,15,17–24]. Modern electrical energy conversion/storage systems can be divided into four groups like

supercapacitors, batteries, electrolysers and fuel cells [1–10,15,18–22]. Supercapacitors and batteries are more suitable for so-called short and medium term electricity storage [1–9,11,12,14,15], respectively. Electrolysers and fuel cells can be used for long term and seasonal electricity storage, i.e. as fuels synthesis devices (hydrogen, methane, etc.) and for regeneration of electricity [9,10,25–28]. Full-cycle efficiency for electrolysers/fuel cells is noticeably lower ($\leq 40\%$ for PEMFC and 70% for SOFC) than that for supercapacitors (95–97%) or different type of batteries (from 60 to 93%) [9,10,25–27]. Thus, in order to construct energetically efficient energy recuperation systems, high performing supercapacitors are of critical importance.

The energy storage characteristics of electrical double layer capacitors (EDLC) are largely determined by the electrical capacitance, system resistance and maximum cell potential. Energy density is proportional to capacitance and is highly dependent on the micro-mesoporous structure (specific surface area (S_{BET}), pore volume (V_{pore}) and pore size distribution characteristics (S_{micro}/S_{meso})) of electrodes under application [1–8,18–24]. However, the power density (P) and energy density (E) are the square functions of the maximum cell potential applied. Thus, the increase of cell potential seems to be the most effective method for enhancement of the EDLC energy and power densities.

The cell potential is limited mainly by the standard potentials of oxidation and reduction of the electrodes. The overvoltage faradic reactions depend mainly on the thermodynamic properties of the solvent and the redox potentials of the electrolyte ions (i.e. decomposition overpotentials) [29]. The series resistance of a two-electrode system is determined by the ohmic drops at the positively and negatively charged electrodes as well as by the mass transfer resistance within the electrolyte layers/volume engaged into the hierarchically porous electrode structure [1,2,18–24]. Additionally, also the porosity and lyophility of a porous separator material, determining the rate of ions transfer through polymeric separator during charging/discharging of EDLC, influences the power density [17,30,31].

The region of ideal polarizability of EDLC depends on the chemical composition of the solvent and electrolyte used. The decomposition overvoltage is usually lower than 1.6 V for neutral aqueous electrolytes ($H_2O + Na_2SO_4$ and $H_2O + Li_2SO_4$) [32,33] or 1.20 V for acid and alkaline electrolytes ($H_2O + H_2SO_4$ or $H_2O + KOH$) [34,35]. For non-aqueous electrolyte based supercapacitors (acetonitrile (AN) + $(C_2H_5)_3CH_3NBF_4$, propylene carbonate (PC) + ethylene carbonate (EC) + $(C_2H_5)_3CH_3NBF_4$, PC + EC + dimethyl carbonate (DMC) + $(C_2H_5)_3CH_3NBF_4$, etc.) the cell potentials usually up to 3.0 V [18–24] can be applied. For EDLC containing ionic liquids like very well cleaned and dried $EtMeImBF_4$, $EtMeImB(CN)_4$, even somewhat higher region of ideal polarizability (up to 3.3 or 3.7 V, respectively) has been demonstrated [36–38]. Also, the further widening of this region of ideal polarizability can be achieved via in-situ/operando deposition of electrochemically (but not ionically) blocking thin film onto porous carbon electrodes [39–41].

AN and PC + EC or PC + EC + DMC mixed solvent systems based electrolytes [4,42] demonstrated somewhat narrower region of ideal polarizability. Kötz et al. [43] established that the insertion of Et_4N^+ into the negatively charged graphite electrode occurs at an onset potential of $+1.0$ V versus Li/Li$^+$. For the positively charged electrode, BF_4^- was shown to intercalate above $+4.3$ V versus Li/Li$^+$. For so-called partially graphitized carbide-derived carbons, the rate of intercalation of Et_4N^+ and even Li$^+$ or Na$^+$ cations is noticeably lower than that at negatively charged graphite electrode [44,45]. In addition, it was shown that addition of some fluorinated [46] and sulphur [47] containing organic solvents into electrolytes somewhat increases (~ 100 mV) the region of ideal polarizability at lower temperature $T < 20\,°C$. However, it should be noted that additions of organic solvents (AN, ethyl acetate, PC, etc.) into RTILs decrease electrolyte viscosity but at the same time cause small narrowing of the region of ideal polarizability [37,38].

The main aim of this paper was to study the electrochemical behaviour of specially pre-treated and partially passivated TiC-CDC electrodes based EDLC at extremely high cell potentials $\Delta E > 3.2$ V, i.e. to analyse the possibilities to increase the energy and power densities of EDLC.

2. Experimental

2.1. Preparation of carbide-derived carbon materials

The experiments were carried out on the thoroughly characterized microporous carbon material obtained by chlorination of titanium carbide [21,48–51]. The titanium carbide (TiC, 99.5% purity, -325 mesh powder, Sigma-Aldrich) was placed into a quartz stationary bed reactor, where it reacted with Cl_2 (AGA, 99.99%) at 1000 °C. The flow rate of Cl_2 was 50 ml min^{-1}. The by-product $TiCl_4$ was led away by the stream of excess Cl_2. During heating and cooling, the reactor was flushed with argon (400 ml min^{-1}). The resulting carbon powder was thereafter treated with H_2 at 900 °C for 1 h to thoroughly dechlorinate the TiC-CDC powder as well as to remove the residual chlorides and oxygen-containing functional groups from the surface of the porous TiC-CDC. This etching technique is a common method to obtain ultra-pure carbide-derived carbon (CDC) materials [4,24,48,49]. The aforementioned synthesis method results in a hierarchically microporous-mesoporous carbon material with small amount of mesopores and a BET surface area of around 1540 m^2 g^{-1} [48,50,51].

2.2. Preparation of electrodes

The supercapacitor electrodes were composed of a mixture of the active TiC-CDC with 5% binder (PTFE, 60% dispersion in H_2O). This mixture was laminated and roll-pressed (HS-160 N, Hohsen Corporation, Japan) together to form a flexible layer of the active electrode material with thickness of $100 \pm 5\,\mu m$. After drying under vacuum, Al current collector (2 μm) was deposited onto one side of the TiC-CDC layer by the magnetron sputtering method. The electrolyte was prepared by mixing of pure acetonitrile (AN, $H_2O < 20$ ppm) and dry $(C_2H_5)_3CH_3NBF_4$ (Stella Chemifa). The two-electrode standard Al test cells (HS Test Cell, Hohsen Corporation) with two identical electrodes (geometric area of about 2.0 cm^2) were completed inside a glove box (Labmaster sp, MBraun; O_2 and H_2O concentrations lower than 0.1 ppm). The carefully dried ($T = 80$ °C, vacuum 50 mbar) 25 μm thick TF4425 (Nippon Kodoshi) separator was used for mechanical separation of the working CDC electrodes. All electrochemical experiments were carried out at 20 °C.

It should be noted that after deposition of the Al layer, the carbon electrodes handled, transported and assembled only in argon atmosphere. The electrodes were not exposed to air at any given time, thus preventing the quick formation of aluminium oxide and adsorption of electrochemically active compounds (H_2O, H_2S, SO_2, CO, CO_2) onto the carbon/Al electrode assembly.

2.3. EDLC characterization methods

The electrochemical characteristics of the completed EDLC cells have been studied by the cyclic voltammetry (CV), constant current charge/discharge (CC) and the electrochemical impedance spectroscopy (EIS) methods, using a SI1287 Solartron potentiostat and 1252A frequency response analyser over a.c. frequency (f) range from 1 mHz to 300 kHz at 5 mV modulation. The constant power method (using a BT2000 testing system, Arbin Instruments, USA) has been used for obtaining the experimental Ragone plots. For passivation of TiC-CDC electrodes the step by step (100 mV) widening of potential region (from 3.0 to 3.7 V) and repetitive (up to 3.4 V) cell potential cycling (up to 2500 times) have been applied.

Infrared spectra before and after electrochemical tests were