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

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HIGHLIGHTS
• Decrease of faradic reaction currents at higher potentials has been achieved.
• Nearly ideal capacitive behaviour (ΔE ≤ 3.7 V) after electrode surface passivation.
• Energy density higher than 30 Wh kg⁻¹ at high power densities 40 kW kg⁻¹.

ABSTRACT
Electrochemical behaviour of titanium carbide-derived carbon (TiC-CDC) electrodes in 1 M (C₂H₅)₃CH₃NBF₄ + 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 (ΔE ≥ 3.4 V) have been measured, comparable even with the sol-gel TiC-CDC/(acetonitrile + (C₂H₅)₃CH₃NBF₄) two-electrode electrical double layer capacitor system. Much higher energy and power values have been achieved at ΔE = 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, electrolyzers 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. Electrolyzers 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 electrolyzers/fuel cells is noticeably lower (≤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_{micr}/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 actions 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 lyophilicity of a porous separator material, determining the rate of ions transfer through polymeric separator during charging/discharging of EDLC, influences the power density [17,20,31].

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_{2}O + Na_{2}SO_{4} and H_{2}O + Li_{2}SO_{4}) [32,33] or 1.20 V for acid and alkaline electrolytes (H_{2}O + H_{2}SO_{4} or H_{2}O + KOH) [34,35]. For non-aqueous electrolyte based supercapacitors (acetonitrile (AN) + (C_{2}H_{5})_{3}CH_{3}NBF_{4}, propylene carbonate (PC) + ethylene carbonate (EC) + (C_{2}H_{5})_{2}CH_{2}NBF_{4}, PC + EC + dimethyl carbonate (DMC) + (C_{2}H_{5})_{2}CH_{2}NBF_{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 EtMeMImBF_{4}, EtMimIm(BCN)_{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_{3}N^{+} 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_{3}N^{+} 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 ΔE > 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 ultrapure 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_{2}O). 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 ± 5 μm. 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_{2}O < 20 ppm) and dry (C_{2}H_{5})_{3}CH_{2}NBF_{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_{2}O 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_{2}O, H_{2}S, 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 potentiotstat 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...
recorded under nitrogen atmosphere with Perkin-Elmer Spectrum GX FT-IR (Fourier-transform infrared) System using ATR configuration [39,52]. Ge hemisphere and IR beam angle of 65° were applied and the Raman spectra were obtained with 514 nm excitation using Renishaw inVia Raman spectrometer. The electrode was placed into a closed argon-filled cell with a glass window.

3. Results and discussion

3.1. Analysis of electrochemical data

Data in Fig. 1 show that for TiC-CDC two-electrode symmetrical cell no quick faradic reactions occurs up to 3.7 V, if the widening of cell potential has been taken by small 100 mV steps. It should be noted that after measuring CVs at each potential window, the charge (CC) and discharge (CD) curves at constant current density were obtained. Thereafter an impedance spectrum was measured, thus after holding the TiC-CDC cell at given maximum potential for ~ 90 min. Comparison of the $C$, $E$ curves measured at different potentials scanning rates $v$ from 5 to 500 mV s$^{-1}$ (Fig. 1c) indicates that the values of $C$ do not decrease noticeably up to $v = 200$ mV s$^{-1}$, demonstrating that only very quick adsorption/desorption step limited reversible processes occur. At $v = 500$ mV s$^{-1}$, there is no ideal shape CVs for TiC-CDC EDLCs, indicating that the absorption equilibrium has not been established. A very good agreement of current (capacitance) values can be seen, independent of the maximum cell potential (up to 3.7 V) applied. Thus, differently from the results of papers [53-57], there is no noticeable quick faradic processes at the electrodes under study in agreement with the results of other works [39-41,52].

The constant current charge/discharge (CC) plots obtained during longer ageing (holding) tests (Fig. 2a) are linear and have symmetrical shape. Notable degradation of EDLC started after holding at maximum cell potential for several hundred hours (250 h), demonstrating nearly 100% coulombic efficiency and from 59% (final state after 400 h) to 93% (initial state) energetic efficiency (Fig. 2b). The energetic efficiency values have been calculated from the integrated energy out/energy in (ratio) values obtained by integration of the discharge/charge curves and the coulombic efficiency values have been calculated using integrated charge density $Q_{out}$ and $Q_{in}$ values and both are given in Fig. 2b. It should be noted that only at very long holding times ($t > 250$ h) energetic efficiency $E_{eff}$ decreases with increasing the holding time applied. The IR-drop values are very low for pre-treated partially passivated cell. IR-drop starts to increase only after polarization at 3.4 V for 300 h (Fig. 2c) in an agreement with CV and impedance data (Figs. 1 and 3).

For detailed analysis, more sensitive electrochemical impedance spectroscopy method has been used (Fig. 3). Based on the analysis of the Nyquist plots ($Z'(\omega)$ vs. $Z''(\omega)$ plots, where $Z'(\omega)$ is the imaginary part of impedance and $Z''(\omega)$ is the real part of impedance) measured at fixed cell potentials, the noticeable deviation from ideal polarizability started at $\Delta E \geq 3.3$ V if the preliminary passivation process has not been used (Fig. 3a). For operando electro-reduction of surface active functional groups, the cell was repetitively charged/discharged up to 3.4 V applying many (from 500 to 2500) CV cycles (Fig. 1d). After CVs, the Nyquist plots were measured and data in Fig. 3a show that, surprisingly, after reaching the cell potentials up to $\Delta E \geq 3.5$ V, deviation from ideal polarizability decreases, and nearly ideal polarizability has been observed for the 2 electrode EDLC system even at $\Delta E = 3.7$ V. For the similar systems, without repetitive CV and CC/CD measurements (Fig. 3b) such passivation effect never occurred, no matter how long the system had been kept at the fixed $\Delta E = 3.4$ V cell potential. Repetitive cell polarization up to $\Delta E \geq 3.4$ V generates the surface conditions, where a system subjected to very high potentials (polarized at $\Delta E \geq 3.5$ V) is much more stable at $\Delta E = 3.4$ V, than a system, which has never been polarized repeatedly at cell potential more than $\Delta E \geq 3.4$ V. The Raman spectroscopy data, discussed later, show that during repetitive polarization up to 3.4 V cell potential the more active amorphous areas (sp$^3$) have been dissolved (oxidized/reduced) from
the TiC-CDC surface [53]. Due to different electrode precondition treatment methods applied somewhat different behaviour of carbon electrodes in non-aqueous and ionic liquid electrolyte based EDLCs have been observed [54–58].

However, data in Fig. 3b (inset) show that during holding and impedance measurements at 3.4 V, the high-frequency series resistance increases nearly 20–25%, indicating that either a thin less conducting film has been deposited onto TiC-CDC electrode surfaces or some morphological changes have taken place in the electrodes (Fig. 3b). In addition, weak increase in resistance (Fig. 3d) can be explained by adsorption of gases onto/into macropores of the TiC-CDC electrodes. It is interesting that the series resistance values \( R_s \) at low frequency \((f = 0.001 \, \text{Hz}) \) only very weakly depend on the cell potential applied (Fig. 3c). Data in Fig. 3e show that the so-called porous material resistance value \( R_s \) usually connected with the mass transfer of ions in mesopores \([1–7,19–24]\), weakly depends on cell potential applied can be explained that there is only weak blocking of mesopores.

This conclusion is in a very good agreement with \( \log|−Z''| \), \( \log f \) plots data [58], presented in Fig. 3f, where two linear regions have been observed: first from 100 to 0.5 Hz (porous region) with \(-0.492 \) slope, i.e. nearly equal to that for ideal semi-infinite mass transfer process (slope \(-0.5\) ), and the second linear region (slope \(-0.992\) ) at lower frequencies (from \( f < 0.5 \) Hz) which is equal to that for ideal adsorption step limited processes (slope \(-1.0\) ).

The shape of the \( \log|−Z''| \), \( \log f \) plots is clearly independent of the cell potential applied. It demonstrates, that the capacitance values are nearly independent of cell potential and CV or CC/CD cycle number applied. Thus, based on Orazem et al. [58] and our previous papers [21,24,30,44,48], the systems under study are ideally polarizable up to 3.7 V, if very careful passivation (pre-treatment of electrodes, i.e. repetitive potential cycling up to 3.4 V and step by step widening of cell potential up to 3.7 V) has been applied. Only at high frequency region, there is increase of \( \log|−Z''| \) values explained by the formation of gases or dielectric layer between carbon electrodes and Al current collectors (mainly positively charged current collector).

The Bode phase angle vs. \( \log f \) plots (Fig. 4) are in an agreement with Nyquist and \( C_s \) vs. \( \log f \) plots shape (Fig. 5). At fixed \( \Delta E = 3.4 \) V, when the system was never subjected to repetitive cell polarization or for CV cycling to higher cell potentials \( \Delta E ≥ 3.5 \) V, the absolute (\( \theta \) ) values decrease at very low \( f ≤ 3·10^{-3} \) Hz (Fig. 4b). However, after some hundred CV and CC/CD cyclization steps and polarizing of the system at potentials \( \Delta E ≥ 3.5 \) V, the absolute values of (\( \theta \) ) started to increase indicating that some passivation (or stabilization) in the cell takes place (Fig. 4a). It is surprising that the cells retain nearly ideal polarizability even up to 3.7 V.

The values of series capacitance

\[
C_s(\omega) = \frac{1}{2\pi f Z'(\omega)}
\]

(1)

and parallel capacitance

\[
C_p(\omega) = \frac{Z''}{2\pi f ((Z'(\omega))^2 + (Z''(\omega))^2)}
\]

(2)

have been calculated and are given in Fig. 5 (\( \omega \) is an angular frequency \( \omega = 2\pi f \)). Long linear plateaus at \( f → 0 \), and overlapping of \( C_s(\omega) \) vs. \( \log f \) and \( C_p(\omega) \) vs. \( \log f \) plots at \( f → 0 \) (Fig. 5b), indicate that equilibrium capacitance values have been established and the systems under study are nearly ideally polarizable up to 3.4 V (without passivation/stabilization) and even up to 3.7 V, if the TiC-CDC electrodes have been carefully passivated/stabilized at \( \Delta E ≥ 3.5 \) V. The \( C_s(\omega) \) vs. \( \log f \) plots have long plateaus at \( f < 1 \) Hz and \( C_s(\omega) \) weakly increases with the cell potential applied (Fig. 5a), explained by the increase of Gibbs adsorption of ions at higher positive and negative surface charge densities.

\( C''(\omega) \), \( \log f \) plots and the characteristic time constant values calculated \((\tau_e = (2\pi f_{\text{max}})^{-1})\), where \( f_{\text{max}} \) is the frequency at the maximum, \( C''(\omega) \), \( \log f \) plots are independent of \( \Delta E \) applied if the TiC-CDC electrodes have been passivated at \( \Delta E ≥ 3.5 \) V. However, the \( \tau_e \) values
weakly depend on the cell potential applied ($\tau_R = 0.84$ s at 3.4 V and $\tau_R = 1.06$ s at 3.7 V) for passivated TiC-CDC cells.

At higher $f \geq 2000$ Hz, some increase in active resistance has been observed (Fig. 3), explained by the increase of contact resistance values between Al current collectors and carbon electrodes, i.e. explained by the increase of thickness of the Al$_2$O$_3$ layer at positively charged current collector [38–41,46–48]. Based on high cell potential and moderate parallel capacitance values ($C_p = 118$ F g$^{-1}$), very high energy and power densities were calculated at $\Delta E \geq 3.4$ V, explained by the deposition of very thin polymeric film at electrode surface.

Fig. 3. Nyquist plots for system subjected (a) to passivation up to 3.7 V, (b) after measurement CV cyclation up to maximum potential 3.4 V. Series resistance $R_s$ vs. log$f$ plots (c) for system subjected to passivation at 3.7 V, (d) for system at fixed cell potential 3.4 V after 2, 1000 and 2500 cycles. (e) Pore resistance $R_{pore}$ vs. cell potential plot for system subjected to passivation for different $\Delta E$ up to 3.7 V at $f = 1$ mHz log $|-Z''|$ vs. log$f$ plots (f) for a passivated system (measured from 0 to 3.7 V), (g) for system at fixed cell potential of 3.4 V, after 2, 1000 and 2500 cycles. $^*$ denotes measurement after reaching 3.7 V (a, c, e) and (1) – (5) in (b) denotes measurement after 500, 1000, 1500, 2000 and 2500 cycles at 50 mV s$^{-1}$. 

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3.2. Experimental Ragone plots

Experimental Ragone plots for the two-electrode EDLC cells completed are given in Fig. 6a, indicating that very high energy and power densities (higher than those for traditional AN based TiC-CDC electrodes) ideally polarizable only up to 3.0 V have been achieved. The $P$ and $E$ values obtained are comparable with corresponding data for sol-gel method synthesized TiC-CDC electrodes and ionic liquid based systems [24,36].

For time-stability analysis, the holding tests have been conducted and the data are given in Figs. 2b, c and 6b. It is very well visible that the cell is more stable after systematic step by step repetitive treatment at high cell potentials ($\Delta E \geq 3.5$ V) than the cell without the special passivation steps. Very stable energy densities at fixed power density have been observed for first 150 h test for electrochemically operando modified electrodes differently from non-passivated TiC-CDC electrodes. The values of $E_{\text{eff}}$ (Fig. 2b) are very high (90%), up to 240 h holding time ($t_{\text{hold}}$) of the two-electrode cell at $\Delta E = 3.4$ V. At longer holding times, $t_{\text{hold}} > 240$ h, some decrease in $E_{\text{eff}}$ takes place. Noticeably quicker decrease of $E_{\text{eff}}$ takes place for the TiC-CDC based cell without operando passivation, i.e. without thin (polymer) layer deposition. The same trend can be seen in Fig. 2c, where increase of IR-drop (obtained from constant current charge/discharge data at $j = 1 \text{A g}^{-1}$) is very low in the case of an operando thin polymer film deposited electrodes based system. However, the quick increase of IR-drop at $\Delta E = 3.4$ V can be seen for the cells with unblocked (without polymer film) electrodes (Fig. 2c), similar to other results [54–57].

3.3. Results of spectroelectrochemical measurements

IR peaks characteristic of CH$_3$CNBF$_3$ and its decomposition products were not noticeable in the IR spectra (Fig. 7) differently from those measured at platinum electrode surface for tetra-n-butylammonium tetrafluoroborate (TBAF) oxidation at $+ 2$ V (vs. Ag wire in 0.01 M...
AgNO₃ + 0.01 TBAF in acetonitrile). Foley et al. concluded that products formed are CH₃CNBF₃ and fluorinated acetonitrile [59]. Our data indicate that at the carbon electrodes the intermediates are either soluble in acetonitrile and therefore have been removed during the electrode washing process before FTIR measurements. Other possible explanations is that only very thin polymeric compound films have been formed at the most active carbon sites, however due to the very low surface concentration, not detectable by FTIR.

Fluorinated carbon IR peaks should appear within the range from ~1000 to 1100 cm⁻¹. However, based on the experimental details, carbon fluorination is unlikely to happen at large extent because it can proceed only at much higher cell potentials than 3.7 V, but never applied in this work [39–41,60]. This effect has previously been tested in the case of EtMelm⁺BF₄⁻ systems [60]. Our present infrared spectroscopy study only identified the anions and/or cations of (C₂H₅)₃CH₃NBF₄ salt in the porous carbon structure. Corresponding signal of BF₄⁻ peaks was stronger at positively charged electrode and, thus, the amount of adsorbed BF₄⁻ ions was larger for passivated positively polarized electrode if compared with negatively polarized electrode data.

Raman spectroscopy data for the passivated positive electrode show increase in the carbon G and 2D peak heights (Fig. 8), thus, indicating some increase in the relative amount of graphitized areas (due to dissolution of sp³ amorphous carbon areas) at the surface of passivated positively polarized carbon grains [53].

It may be concluded that careful repetitive overvoltage treatment at ΔE ≥ 3.5 V causes dissolution (through many oxidation/reduction steps) of some amorphous sp³ areas from the TiC-CDC surface and (relative) increase in the graphitic sp² carbon areas (Fig. 8). This effect has been systematically established in all 4 experiments conducted under identical experimental conditions, thus these results are statistically reproducible. Similar effects were not observed at negatively passivated electrodes, and also when the maximum potential did not exceed 3.2 V.

Possibly the electrochemical oxidation/reduction reaction at high cell potentials eliminates electroactive surface trace groups at the porous carbon TiC-CDC surface, such as –Cl, -H, OH, =O, Si, Fe, etc. [39–41,60–62]. Remaining cleaned TiC-CDC surface is more graphitic, thus electrochemically less active [53] and higher cell potentials can be applied to the EDLC cell without initiating fast faradic processes.

Due to reduction reactions and probable gas evolution taking place at negatively overcharged electrode at ΔE > 3.7 V, probably the Teflon binder degenerated at more high negative surface charge densities [54–57,61,62]. Thus, there is slow hydrogen evolution at negatively overcharged electrode [36–41,52,61,62], but only soluble (or very thin film) compound formation at positively overcharged electrode, which explains why negatively charged electrode starts degrading faster than the positively charged electrode at cell potentials ΔE ≥ 3.7 V.

4. Conclusions

It was demonstrated that it is possible to stabilize the EDLC based on TiC-CDC electrodes in 1 M (C₂H₅)₃CH₃NBF₄ + acetonitrile at cell potentials higher than 3.4 V if careful electrochemical pre-treatment of the system (step by step widening of potential cycling region and repetitive CV polarization up to 3.7 V) has been applied. More detailed analysis of CV and impedance spectroscopy data shows that nearly ideal capacitive behaviour up to ΔE = 3.7 V has been achieved (phase angle more negative than −86°), however only for the system previously subjected to step by step widening of potential scanning region (wider than ΔE ≥ 3.4 V). The passivation effect can be explained by oxidation-reduction (electrochemical elimination) of the more amorphous and active sites CV, i.e. electrochemical dissolution of more active carbon sites from TiC-CDC surface and enrichment of the surface with more stable graphitic sp² regions or by formation of the thin passive polymeric films. The exact mechanism for the stabilization/passivation phenomenon cannot be determined in this work, but should definitely be studied in more detail using long-lasting cell potential cycling experiments applying in situ FTIR or by secondary ion mass spectrometry and synchrotron radiation based XPS methods. EDLCs with such high cell potential might not have the same very long-lasting stability as the current commercial supercapacitors (cell potential lower than 3.0 V), but they surpass the commercial EDLCs significantly in energy and power densities. These EDLCs can be used for applications, where the extremely high power densities are inevitable.
Fig. 8. Raman spectra of (a) regular, positively and negatively charged electrode at 3.2 V, and positively and negatively charged electrode passivated at 3.7 V (b), (c) and zoomed in.

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References


