Novel sol-gel synthesis route of carbide-derived carbon composites for very high power density supercapacitors

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abstract

Sol-gel synthesis process was applied to obtain titanium carbide and titanium carbide/carbon nanotubes composites. These materials were used as precursors for the synthesis of carbide-derived carbon materials for supercapacitor electrodes. The results of X-ray diffraction, scanning electron microscopy and Raman spectroscopy showed that the synthesized CDC materials have average dimensions from 10 to 50 μm and are dominantly amorphous with some relatively small graphitic crystallites inside particles. The low-temperature sorption experiments were performed and the specific DFT surface area up to 276 m² g⁻¹ for the synthesized carbides and up to 1710 m² g⁻¹ for carbon composites were obtained. Compared to traditional titanium carbide-derived carbons the materials exhibit larger specific DFT surface areas and a unique pore size distribution with more mesopores between 2 and 10 nm.

The energy-related properties of the supercapacitors based on the synthesized carbon materials in 1 M (C₂H₅)₃CH₃NBF₄ solution in acetonitrile were investigated using the cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge/discharge methods. The materials demonstrate nearly ideal capacitive behavior even at very high charging/discharging currents (10 A g⁻¹) and potential scan rates (500 mV s⁻¹). The Ragone plots have been calculated from constant power tests, demonstrating high gravimetric energy densities (20 Wh kg⁻¹) at high power densities (200 kW kg⁻¹).

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EDLCs allow them to complement or replace batteries and fuel cells in applications, where the high power and energy densities are important such as peak power sources, hybrid electric vehicles, space devices, digital communication devices, mobile phones and industrial applications [5,13,14].

The unique nanoporous structure of carbide-derived carbon (CDC) with the narrow pore size distribution and possibility to fine-tune the pore size and volume has given them great potential to be used as electrode materials in EDLCs and other devices [2,6–8,15–23]. Comprehensive review as an electrode material has been completed by Oschatz et al. [24]. CDC powders, produced by selective etching of metal carbides in a chlorine-containing environment, offer narrow distribution of micropores. However, although CDCs can have high energy and power densities, great effort is put into increasing these values even further [9]. For example, the power densities can be increased by either additional activation or templating the carbon material, which results in creating bigger mesopores for quick mass transport. Additionally, it is quite common to physically mix materials into the electrodes to increase conductivity or porosity [25,26]. Another option is to increase the energy densities by complex hybrid systems where small particles or thin films of pseudocapacitive materials are used [27,28]. First synthesis of TiC using titanium butoxide has been conducted in 2010 [29] and thereafter the TiC has been used for synthesis of TiC-CDC with well determined characteristics [30–32]. Recently sol-gel method has been used for synthesis of Nb-CDC from niobium butoxide [29–33]. Sol-gel method also gives the possibility of adding carbon nanotubes to the precursor carbide material during the sol–gel carbide synthesis process, which should ensure better connections between the carbon and the carbon nanotubes and induce a more uniform additional mesoporosity throughout the material.

Since Iijima first reported fabrication of the multiwall carbon nanotubes (CNT) more than twenty years ago, they have become an important industrial material for many applications. Due to their high mechanical strength (Young's modulus up to 950 GPa), excellent electrical and thermal conductivity, CNTs are a promising component to design multifunctional materials and components for various devices [34]. CNTs, as well as their composites, have been used in various areas of technology, such as reinforced materials, nanoscale electronic devices, hydrogen storage and field emission materials and electrodes for electrochemistry [34–39]. CNTs have been used as reinforcement in polymer [40–42], metal [43–45], and ceramics composites [35,36,46,47] of CNT-polymer composites. Remarkable enhancements have been achieved in mechanical properties in composites, compared to monolithic materials. Detailed analysis demonstrates that in ceramic matrix composites the advancements have not been so remarkable as for polymer matrix composites [48].

Few reports have been published about synthesis of bigger particles of refractory carbides/CNT composites [49,50]. Morisada et al. [51] reported the increase of Vickers hardness and fracture toughness by adding SiC-coated CNTs to SiC matrix. Wang et al. [52] produced multi-walled carbon nanotube-reinforced silicon carbide ceramic fibers. In these studies, the main aim was to increase the mechanical properties of carbides.

To synthesize high quality CNT ceramic matrix composites, it is necessary to solve three critical issues: 1) guarantee homogeneous dispersion of CNTs in the matrix system, 2) optimize the interfacial bonding strength between CNTs and adjacent matrices and 3) develop a novel consolidation method that do not damage the CNTs. It is crucial that the carbon nanotubes are homogeneously dispersed in the material matrix as the presence of agglomerates can act as a defect points leading to the material failure [53].

Sol–gel technology has shown outstanding results for syntheses of metal oxides [54,55], metal carbides [56,57] and metal oxide/CNT composites with advanced characteristics [53,58,59]. In the sol–gel method CNTs dispersion and liquid matrix precursors are mixed at molecular level which allows homogeneous CNTs dispersion and a molecular interaction with ceramic matrix [60,61]. Sol–gel technology is a versatile technology, making it possible to produce a wide variety of materials formations like powders, fibers, coatings and monoliths [62,63].

In our present work sol-gel technology has been used to synthesize homogeneous TiC and TiC/CNT precursors for carbide-derived carbon synthesis. Samples with two different CNT wt% (1% and 2%) concentrations were prepared to study the possibilities of improving the electrochemical properties of the resulting carbide-derived carbon materials.

2. Experimental

2.1. Sol–gel synthesis and preparation of the carbide precursors

Titanium(IV)butoxide, (Ti(OC4H9)4, 99% purity, Alfa-Aesar), was used as metal source and benzene-1,4-diol, (C6H4(OH)2, 99% purity, Sigma-Aldrich), as a carbon source. CNTs used were 10–30 µm long and their outer diameter was 10–20 nm (95 wt%, CheapTubes Inc.). Polyvinylpyrrolidone, ((C6H9NO)n, avg. M = 1 300 000 g mol−1, Sigma-Aldrich), was used as a surfactant for better dispersion of the CNTs. 1-butanol, (C4H10OH, ≥ 99.7% purity, Sigma-Aldrich), was used as a solvent, where CNTs were dispersed using polyvinylpyrrolidone (PVP) as a surfactant. The molar ratio of surfactant/CNTs was 10:1. Two different mixtures were made: 1 wt% and 2 wt% CNTs in C4H10OH (weight percentage from carbide's final mass). All mixtures were treated with an ultrasonic probe (UP 2005) for three hours.

For the preparation of TiC sol precursor Ti(OC4H9)4 was dissolved in 1-butanol in argon environment in a three-neck flask at 50 °C. After that the CNT dispersion was added into the Ti(OC4H9)4 solution, followed by an ultrasonic treatment with an ultrasonic bath (Elmasonic P 30H, frequency 37 kHz) for one hour to disperse CNT homogeneously in the titanium alkoxide solution. The ultrasonically treated mixture was heated up to 80–100 °C for adding extra carbon source benzene-1,4-diol, dissolved in ~25 ml 1-butanol. Ti(OC4H9)4 and C6H4(OH)2 molar ratio was 1:0.55. Benzene-1,4-diol in 1-butanol was added dropwise to prevent the premature gelation and dissolve all benzene-1,4-diol in sol. The obtained sol was heated at 105–115 °C for 2.5 h for the transesterification and polycondensation reactions to be completed. 1-butanol was removed by applying distillation at T > 120 °C and the xerogel received was dried completely. The dried sample was grinded into a homogeneous powder by a magnetic stirrer. Fig. 1 demonstrates the synthesis process carried out.

Three samples with different CNT concentrations were prepared including TiC precursor without CNTs (as a reference material), TiC/1wt% CNT and TiC/2wt% CNT. The PVP will decompose during carbothermal reduction to amorphous carbon. Concentration of PVP is quite low compared to the TiC concentration and it should not give unnecessary free carbon in synthesis products. PVP formed a reversed micelle around CNT, the molecular chain of the PVP adsorbed and wrapped on the CNTs randomly and ultrasonic treatment provided strong shearing forces between CNTs. CNTs covered with such polymers could react with polycarbosilane titanium(IV)butoxide by benzene-1,4-diol, and CNT surface have been coated with shell of TiC precursor. Such shells should form through hydrogen bonding interaction between a carbonyl group of PVP chains and the hydroxyl group results from the polycarbosilane reaction of titanium(IV)butoxide [64,65]. Due to the mentioned processes the PVP behave as a polymer glue between CNT and TiC precursors.
Titanium(IV)butoxide in 1-butanol

Dissolution at 50 °C

Solution of metal butoxide

Addition of CNT dispersion

CNT dispersion in 1-butanol

Titanium(IV)butoxide-CNT solution

Heating at 80-100 °C

Black solution

Reaction at 105-115 °C

Distillation of 1-butanol above 120 °C

TiC-CNT precursor xerogel

Fig. 1. Block scheme of the experimental procedure used for the fabrication of precursor carbides.

2.2. Preparation of carbide-derived carbon materials

The synthesized TiC-CNT composites were placed onto a quartz stationary bed reactor and reacted with a steady flow of Cl₂ (AGA, 99.99%) at T = 950 °C. Details of the etching technique have been reported previously [66–68]. The flow rate of Cl₂ was fixed at 50 ml min⁻¹. During heating up and cooling down steps, the reactor was flushed with argon (300 ml min⁻¹). The pyrolyzed samples were carbothermally reduced at 1350 °C in vacuum at 7·10⁻² mbar in a tube furnace (WEBB 107) and the carbothermal reduction at the maximum temperature was 60 min. The heating rate was adjusted to 200 °C h⁻¹.

2.3. Characterization methods applied

The samples were analyzed with X-ray diffraction (XRD) method. The diffractograms were recorded using CuKα radiation (45 kV, 35 mA, λ = 0.154056 nm) with a step size 0.01° of glancing angle θ and with the holding time of 2 s at fixed θ on Bruker D8 Advance diffractometer (Bruker Corporation). The structures of the samples were studied using a scanning electron microscope (SEM) FEI Helios Nanolab 600. The samples were also analyzed with Raman spectroscopy, using spectrometer Renishaw micro-Raman (setup equipped with 514 nm continuous mode argon ion laser, (laser power 1.3 mW) and the spectral resolution was approximately 1.5 cm⁻¹.

For the characterization of porosity and surface area of the carbide and carbon materials, low-temperature nitrogen and carbon dioxide sorption methods were used. The N₂ and CO₂ sorption measurements were performed using 3FLEX (Micromeritics) and ASAP2020 (Micromeritics) systems, respectively. The specific surface area, S_{BET}, was calculated according to Density Functional Theory (as well as using BET model only for better comparison of data with previously published ones) [69,70]. Pore size distributions have been calculated by applying non-local density functional theory to N₂ adsorption isotherms and CO₂ adsorption isotherms applying program: Solution of Adsorption Integral Equation Using Splines (SAIEUS, Micromeritics). The models used for pore size distribution calculation were Carbon-N2-77, 2D-NLDFT Heterogeneous and Carbon-CO2-273, 2D-NLDFT Het Surface. [71,72].

2.4. Preparation of electrodes

The supercapacitor electrodes were composed of an aluminum current collector and a mixture of the synthesized CDC material and a binder (PTFE, 60% dispersion in H₂O). The binder content was 6 wt%. This mixture was laminated and roll-pressed (HS-160 N, Hothesen Corporation, Japan) together to form a flexible layer of the active electrode material with a thickness of 150 ± 5 μm. After drying under vacuum, the pure Al layer (2 μm) was deposited onto one side of the CDCs by magnetron sputtering method. It should be noted that the vacuum deposited Al layer is very useful for current collection especially for very high power density EDLCs [73]. For electrochemical measurements, the two-electrode standard Al test cell (HS Test Cell, Hothesen Corporation) with two identical electrodes (geometric area of about 2.0 cm²) was completed inside a glove box (Labmaster sp, MBraun; O₂ and H₂O concentrations lower than 0.1 ppm). The carefully dried 25 μm thick TF4425 (Nippon Kodoshi) separator sheet was used for mechanical separation of the working CDC electrodes. All electrochemical experiments were carried out at temperature T = 20 °C.

Electrochemical characteristics of the EDLCs, consisting of the synthesized carbon electrodes and 1 M (C₆H₅)₃CH₂NB₄(TEMABF₄) in acetonitrile (AN), have been studied by cyclic voltammetry, constant current charge/discharge and the electrochemical impedance spectroscopy methods using a SI1287 Solartron potentiostat and 1252A frequency response analyzer over ac frequency, f, range from 1 mHz to 300 kHz at 5 mV modulation. Constant power tests were performed on a BT2000 testing system (Arbin Instruments, USA). The general measurement setup is given in Supplementary material.

3. Results and discussion

3.1. Physical characterization

From the SEM analysis data, it was possible to determine that the materials synthesized have a wide particle size distribution (Fig. 2a–d). The synthesized carbide particles observed have average dimensions around 10 μm, while material particles with CNT additions have larger (around 50 μm) (Fig. S1, Supplementary material). The bigger particle dimensions of carbides with CNT additions can be explained by the relatively long CNT lengths (10–30 μm), which probably stabilize the bigger particles and holds them together. It can be seen that partially bundled carbon nanotubes are indeed visible on the surface of the carbon particles (Fig. 2d). While occasional separate CNTs can be seen in the material with 1% CNTs (Fig. S2, Supplementary material), the material with 2% of CNTs demonstrates small bundles of CNTs, thus indicating that for materials with higher CNTs additions (2%) the dispersion of nanotubes was not sufficient (Fig. 2d).
The XRD diffractograms, presented in Fig. 3, demonstrate the formation of TiC (111 and 200 reflections) after carbothermal reduction process. Additionally the material containing 2% CNTs also exhibits very small reflection near 25 – 26°, which can be related to the 002 peak of graphitic carbon (CNT). However, additional XRF measurements conducted on the samples showed that the materials under study contain 11–13 wt% oxygen (Table. S1, Supplementary material). Due to the fact that titanium carbide and titanium oxycarbide have nearly the same lattice parameters, it was not possible to determine the exact stoichiometry of the synthesized TiO_{x}C_{1-x}/TiC materials based on the XRD measurements conducted. It has been shown by other authors that the exact stoichiometry depends noticeably on the carbothermal treatment temperature and duration [74–76]. However, even though the carbothermal reduction process did not lead to a fully stoichiometric TiC, the CDC materials obtained after the high temperature.
chlorination process exhibit a classical XRD diffractograms (Fig. 3b) and Raman spectra (Fig. 3c) characteristics of the highly disordered micro-mesoporous carbons [66–68]. It can be seen (Fig. 3b and c) that the addition of CNTs leads to a slight increase in the ordering of the carbon matrix, established by the formation of 002 peak in the diffractograms [66–68,77,78]. However, it should be noted that it is not possible to distinguish the reflections resulting from CNTs and mesopores. The DFT (given in Table 1) (and BET values given in Table 1) show that both the initial carbide and different mixtures and the final carbon materials synthesized have micropores and mesopores. The DFT (given in Table 1) (and BET values given only for comparison) specific surface area values of the carbides increase from 152 to 276 m² g⁻¹, in correlation with works of other authors [79]. The synthesized CDCs had a noticeably higher DFT specific surface area values up to 1710 m² g⁻¹, which is noticeably higher than that normally obtained for TiC-CDC [17,79]. It should be noted that the addition of CNTs into TiC decreases the overall surface area, even though the pore size distribution remains mostly unchanged. It is possible that the general increase in mesoporosity and DFT surface area in all materials under study is caused by the oxygen, left inside the material as titanium oxycarbide (TiOxC₁−ₓ), reacting with the carbon formed during the high temperature treatment step and therefore creating a more porous structure. Additionally, some mesoporosity is originating from the sol-gel synthesis process evident of the pore size distributions of the carbides. It should be noted that classical BET values are 10–15% higher than DFT values, thus slightly overestimated.

The adsorption isotherms and pore size distribution data (Fig. 4) show that both the initial carbide and different mixtures and the final carbon materials synthesized have micropores and mesopores. The DFT (given in Table 1) (and BET values given only for comparison) specific surface area values of the carbides increase from 152 to 276 m² g⁻¹, in correlation with works of other authors [79]. The synthesized CDCs had a noticeably higher DFT specific surface area values up to 1710 m² g⁻¹, which is noticeably higher than that normally obtained for TiC-CDC [17,79]. It should be noted that the addition of CNTs into TiC decreases the overall surface area, even though the pore size distribution remains mostly unchanged. It is possible that the general increase in mesoporosity and DFT surface area in all materials under study is caused by the oxygen, left inside the material as titanium oxycarbide (TiOxC₁−ₓ), reacting with the carbon formed during the high temperature treatment step and therefore creating a more porous structure. Additionally, some mesoporosity is originating from the sol-gel synthesis process evident of the pore size distributions of the carbides. It should be noted that classical BET values are 10–15% higher than DFT values, thus slightly overestimated.

3.2. Analysis of electrochemical data

The cyclic voltammograms (CVs) were measured within various electrode potential regions ΔE (up to 3.4 V) at potential scan rates (ν) from 2 to 500 mV s⁻¹. The medium capacitance (CₘCV = Δq/ΔE) values have been calculated over the cell potential range ΔE from 0 to 3.0 V using the integrated total charge density q values, obtained according to Eq. (1):

\[ q = \int_{E_1}^{E_2} i(ΔE) \, dt = \int_{E_1}^{E_2} \frac{i(ΔE)}{E} \, d(ΔE). \]  

Eq. (1) can be used to calculate the capacitance values only within the region of moderate cell potential scan rates, if the values of current, i, are small, as only in these conditions the potential drop (IR-drop) is negligible. Only under these conditions the current response is essentially equal to that of a pure capacitor [80–83]. In a symmetrical two-electrode system the specific capacitance Cₘ (F g⁻¹) for one activated carbon electrode can be calculated as follows:

\[ C_m = \frac{2C}{m}, \]  

where m is the weight in g cm⁻² per one activated carbon electrode, assuming that the positively and negatively charged electrodes have the same capacitance at fixed ΔE.

The specific capacitance (CₘCV) (calculated from CV data) vs. cell potential (ΔE) curves for all samples studied are presented in Fig. 5a–d. The CₘCV vs. ΔE curves (Fig. 5a and b) demonstrate that there is small, but clearly recognizable dependence of CₘCV on the CNT fraction in the TiC-CDC powders. This could be explained by the specific surface area differences or that the pores or surfaces formed due to the inclusion of CNTs are not suitable for the formation of the electric double layer [81]. All sol-gel Ti-C-CDC synthesized materials based EDLCs demonstrate practically ideal capacitive behavior at cell potential scan rate ν ≤ 500 mV s⁻¹ and up to ΔE ≤ 3.4 V (Fig. 5b and c) in TEMABF₄ in AN. Data of 10 and 100 repetitive cycles are given in Fig. S3. However, it should be noted that although the CV curves exhibit ideal capacitive behavior at very high potentials, their application is limited as shown later by analysis of impedance spectroscopy data. Nevertheless, these materials show one of the best capacitive behavior at potentials over 3.2 V in TEMABF₄ in AN. Such high potential scan rates, while retaining good capacitive behavior have been previously obtainable only via different methods involving templating

![Image](Fig. 4. Low-temperature N₂ adsorption/desorption isotherms for porous TiC and additions of carbon nanotubes (noted in Figure) (a), for the prepared carbide-derived carbons (noted in Figure) (b), Differential pore size distribution vs. pore width plots, obtained using NLDFT method for titanium carbide and with additions of carbon nanotubes (c), and for the prepared titanium carbide-derived carbons (d) (noted in Figure).)
of CDC materials or electrospinning [25,84–86]. This indicates that even at such high potential scan rates \( \eta = 500 \text{ mV s}^{-1} \), there is no significant potential drop arising from the slow mass-transfer step in the porous CDC matrix. This is probably due to the extra generated mesoporosity, because the sol–gel synthesis method provides additional pores in the range from 4 to 10 nm.

The calculated specific capacitance values are given in Table 2. The capacitance values depend slightly on the extent of CNT fraction in the TiC-CDC, and surprisingly the addition of CNTs decreases weakly the capacitance values, thus being in correlation with the \( S_{\text{DFT}} \) and \( V_{\text{micro}} \) values (Tables 1 and 2). The highest integrated specific capacitance value \( C_{\text{int,CV}} = 112 \text{ F g}^{-1} \) has been obtained for material prepared from pure TiC-CDC at \( \eta = 10 \text{ mV s}^{-1} \). When the potential scan rate is increased up to \( \eta = 500 \text{ mV s}^{-1} \), this material still maintains a very high specific capacitance value \( C_{\text{int,CV}} = \sim 106 \text{ F g}^{-1} \).

The supercapacitors were tested at constant current charge/discharge regimes \( (j=1 \text{ A g}^{-1}, j=5 \text{ A g}^{-1}, j=10 \text{ A g}^{-1}) \) at the cell potentials from 0 to 3.0 V (Fig. 6), which correlates to the maximum potential limit of most commercially available supercapacitors.

The constant current (CC) charge-discharge curves for the synthesized materials are nearly linear and symmetrical at all current densities \( (1–10 \text{ A g}^{-1}) \), showing very good electrochemical reversibility, energetic and coulombic efficiency (Table 3) of the cells completed. At different current densities \( (1 \text{ A g}^{-1}, 5 \text{ A g}^{-1}, 10 \text{ A g}^{-1}) \) the charging curves are nearly linear, thus indicating that there is no significant contribution of the slow mass-transfer inside of the porous carbon electrode.

Due to the fact that the CC plots are very weakly non-linear the specific energy densities have been calculated using integration method and the results calculated are given in Table 3.

The cycling efficiency, i.e., the so-called round trip efficiency (RTE) (Table 3) has been calculated as a ratio of charges released and accumulated \( (Q_{\text{charge}}/Q_{\text{discharge}}) \) during discharging and charging of the supercapacitors. The calculated RTE values for all synthesized carbon based systems exceeded 99% for all materials based

<table>
<thead>
<tr>
<th>Sample</th>
<th>DFT specific surface area of precursor carbide ((\text{m}^2\text{g}^{-1}))</th>
<th>DFT specific surface area of carbon ((\text{m}^2\text{g}^{-1}))</th>
<th>BET specific surface area of precursor carbide ((\text{m}^2\text{g}^{-1}))</th>
<th>BET specific surface area of carbon ((\text{m}^2\text{g}^{-1}))</th>
<th>Total pore volume ((\text{cm}^3))</th>
<th>T-plot micropore surface area ((\text{m}^2\text{g}^{-1}))</th>
<th>T-plot mesopore pore volume ((\text{cm}^3\text{g}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC-CDC</td>
<td>244</td>
<td>1710</td>
<td>290</td>
<td>2150</td>
<td>2.85</td>
<td>280</td>
<td>2.74</td>
</tr>
<tr>
<td>TiC/1%CNT-CDC</td>
<td>152</td>
<td>1560</td>
<td>160</td>
<td>2000</td>
<td>2.99</td>
<td>283</td>
<td>2.88</td>
</tr>
<tr>
<td>TiC/2%CNT-CDC</td>
<td>276</td>
<td>1510</td>
<td>320</td>
<td>1790</td>
<td>2.94</td>
<td>340</td>
<td>2.81</td>
</tr>
</tbody>
</table>

Fig. 5. Specific capacitance vs. cell potential curves calculated from CV curves at potential scan rates: \( \eta = 10 \text{ mV s}^{-1} \) (a), \( \eta = 500 \text{ mV s}^{-1} \) (b) for the supercapacitors, completed using TiC-CDC, TiC/1%CNT-CDC and TiC/2%CNT-CDC as electrodes, and at scan rate \( \eta = 20 \text{ mV s}^{-1} \) with different potentials for supercapacitors, completed using TiC-CDC (c) and TiC/1%CNT-CDC as electrodes (d).

Table 2
Calculated specific capacitance values from cyclic voltammetry data \((\Delta \text{E} = 3 \text{ V}; \eta = 10 \text{ mV s}^{-1}; \eta = 100 \text{ mV s}^{-1}; \eta = 500 \text{ mV s}^{-1})\), and impedance spectroscopy measurements \((\Delta \text{E} = 3 \text{ V}; f = 1 \text{ mHz})\) for the materials under study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cyclic voltammetry</th>
<th>Impedance spectroscopy 3 V ((\text{F g}^{-1}))</th>
<th>Time constant (\tau) ((\text{s}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 mV s(^{-1}) ((\text{F g}^{-1}))</td>
<td>100 mV s(^{-1}) ((\text{F g}^{-1}))</td>
<td>500 mV s(^{-1}) ((\text{F g}^{-1}))</td>
</tr>
<tr>
<td>TiC-CDC</td>
<td>112</td>
<td>111</td>
<td>106</td>
</tr>
<tr>
<td>TiC/1%CNT-CDC</td>
<td>104</td>
<td>103</td>
<td>100</td>
</tr>
<tr>
<td>TiC/2%CNT-CDC</td>
<td>93</td>
<td>92</td>
<td>89</td>
</tr>
</tbody>
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established indicates the adsorption limited process inside porous electrodes [9,17].

The phase angle, $\theta$, vs. $ac$ frequency dependencies for the EDLCs completed with the prepared electrodes in TEMABF$_4$ in AN are presented (Fig. 7b and Table S3). For all synthesized materials at $f \leq 0.1$ Hz, the phase angle $\theta$ was nearly $-90^\circ$, demonstrating the truly capacitive behavior of systems under study. The phase angle values start to increase with increasing the cell potentials $\Delta E \geq 3.3$ V as a result of the beginning of very slow faradaic reactions at the highly negatively and positively charged electrodes, thus at very high cell potentials applied.

The specific series capacitance, $C_s$ values have been calculated from the impedance spectroscopy data at $ac$ frequency $f = 1$ mHz (Fig. 7c and Table 2). The highest capacitance value of 139 F g$^{-1}$ at 3 V has been established for TiC-CDC [9,87,88]. Again, this could be explained by the specific surface area differences or that the pores or surfaces formed due to the inclusion of CNTs are not suitable for the formation of the electric double layer [81].

According to electrochemical characterization, the high frequency series resistance $R_s$, so-called pore resistance $R_{pore}$, and constant phase element (CPE) fractional exponent values $\alpha$ at $f = 5$ mHz were calculated, indicating that the different samples have quite similar electrochemical properties (Table S3). Only the $\theta$ and $\alpha$ values start to increase or decrease, respectively, showing some deviation from ideal capacitive behavior of TiC/2%CNT-CDC electrodes.

For more detailed analysis, the values of complex power can be expressed as

$$S(\omega) = P(\omega) + jQ(\omega)$$

where the active power $P(\omega)$ is expressed as

$$P(\omega) = \omega C(\omega)|\Delta E_{rms}|^2$$

and the reactive power $Q(\omega)$ is expressed as

$$Q(\omega) = -\omega C(\omega)|\Delta E_{rms}|^2$$

with $|\Delta E_{rms}|^2 = \Delta E_{max}/\sqrt{2}$ ($\Delta E_{max}$ is the maximum amplitude of $ac$ potential, 5 mV). In the case of an ideal capacitor (i.e. a system with the ideal capacitive behavior), there is no real part as there is only the reactive contribution to the complex power. In this case, Eq. (3) simplifies to

$$S(\omega) = jQ = -\frac{j\Delta E_{rms}^2}{|Z|} = -j\omega C\Delta E_{rms}^2.$$

Systems with ideal resistive behavior have no imaginary part and the equation for complex power takes the form

$$S(\omega) = \frac{\Delta E_{rms}^2}{|Z|}.$$
It should be noted that the real supercapacitors balance between these two states mentioned: resistive at high frequencies ($f \to \infty$) and capacitive at low frequencies ($f \to 0$). Between these two limiting states supercapacitor behaves like an RC-transmission circuit [1,5,6,11,88–90]. The dependence of the normalized real part ($|P|/|S|$) and imaginary part ($|Q|/|S|$) of the complex power on $ac$ frequency are presented in Fig. 7d. Characteristic charging/discharging time constant $\tau$ values, given in Fig. 7d, have been determined from the frequency of interception points $f_{int}$ of the $|P|/|S|$ and $|Q|/|S|$ curves according to Refs. 1,89,90

$$\tau = \frac{1}{2\pi f_{int}}. \quad (8)$$

Extremely short characteristic time constants $\tau$ indicate that synthesized materials can be used for completing of very high power density supercapacitors. However, it should be noted that the relaxation time constant is a parameter that can somewhat change from cell to cell. The time constant depends both on the cell capacitance, but also on the cell resistance, the latter being mainly affected by the contact resistance between the electrode and the current collector, which probably varies between the cells used by different workgroups and are, thus, not always very comparable. However, in our work very high capacitance values indicate that the resistance values are very small in an agreement with data dismissed above, thus, very high power densities at high energy densities can be expected. Also, data for comparison of the TiC-CDC capacitance values derived in this work with other TiC-CDC electrodes indicate that TiC-CDC materials synthesized via sol-gel technology have higher or comparable specific capacitance values (Table S4).

The experimentally measured gravimetric Ragone plots (specific energy, $E$, vs. specific power, $P$, dependencies) calculated to the total material weight of two electrodes (for the supercapacitors based on different synthesized electrodes) have been obtained from the constant power tests within the cell potential range from 3.0 V to 1.5 V (Fig. 8a and c) and 3.2 V to 1.6 V (Fig. 8b and d) [1,91]. The Ragone plots measured for single cells completed from the materials synthesized show weak influence of the CNT fraction in the carbon powder on the stored specific energy and power values delivered. It should be pointed out that extremely high power densities $P=200\ kW\ kg^{-1}$ at high energy density $E=20\ Wh\ kg^{-1}$ have been measured for the synthesized TiC-CDC (without addition of CNT) as well as for 1 wt% CNT in TiC-CDC. For 2 wt% CNT in TiC-CDC the energy and power densities are 2 times lower. Comparison with single cells data, completed from carbon powders prepared from commercial WC and TiC powders by high temperature chlorination indicates that sol–gel method based systems based carbon powder are able to generate higher power densities especially at high energy [17,77,83,92]. In Fig. 8c and d the volumetric energy density power density plots are given, indicating that TiC-CDC materials based single cell are able to generate extremely high volumetric power densities at high volumetric energy densities. It should be noted, that in this paper, there was no additional pressuring or densification of the electrodes carried out in order to increase the volumetric energy and power densities.

The combined durability testing method used is shown schematically in Fig. 9a [93]. After cyclic voltammetry measurements (Fig. 9b) and 500 galvanostatic charge/discharge cycles (1 A g$^{-1}$) within potential regions from 0 to 3.0 V (Fig. 9c) and 10 h holding of cell at 3.0 V, the impedance spectra were measured at 3.0 V (Fig. 9d). Results in Fig. 9b indicate that there is very slow decrease of cell capacitance calculated from cyclic voltammograms (from 130 to 125 F g$^{-1}$) as well as shortening of charging/discharging times 5–10% (Fig. 9e). The Nyquist plots shape is practically independent of cycle numbers applied, however very small increase of series resistance (6–7%) from 0.28 to 0.30 $\Omega\ cm^2$ takes place (inset in Fig. 9d). According to series capacitance, $C_s$, and parallel capacitance, $C_p$, calculations (Fig. 9e and f) the capacitance values decrease less than 15% during 2500 constant current charge/discharge cycles (total number) and 50 h (total holding) applied. Throughout the durability test the electrode material demonstrated nearly ideal capacitive behavior.

Analysis of this study proved that synthesizing TiC-CDC particles via sol-gel method results in very attractive electrochemical behavior of the material when used as supercapacitor electrodes. Even though the addition of carbon nanotubes did not enhance
the electrochemical properties, it is shown that the carbon nanotubes can be introduced into the CDC material through the provided synthesis method. Thus, sol-gel synthesis method can be used to incorporate other novel materials inside the CDC by the reaction steps provided or using additional mechanisms such as catalytic chemical vapor deposition to incorporate graphene.

Fig. 8. Gravimetric and volumetric Ragone plots for supercapacitors completed using TiC-CDC, TiC/1%CNT-CDC and TiC/2%CNT-CDC, and CDCs synthesized from commercial WC [77] and TiC [17], measured between cell potentials 3.0 V to 1.5 V (a and c) and 3.2 V to 1.6 V (b and d).

Fig. 9. The electrochemical durability test’s measurement setup cycle (N) (a). Cyclic voltammograms (b), constant current charging/discharging curves (c), Nyquist plots (d), series capacitance, $C_s$ (e) and parallel capacitance, $C_p$ (f) vs frequency plots measured at cell potential $\Delta E = 3.0$ V.
4. Conclusion

The sol-gel synthesis process was applied to prepare the titanium carbide (TiC) and titanium carbide/carbon nanotubes (CNT) composites. Samples with two different CNT wt% (1% and 2%) concentrations were prepared to study the possibilities of improving the electrochemical properties of the resulting carbide-derived carbon materials. Synthesized materials were used as precursors for the preparation of carbide-derived carbon materials for supercapacitor electrodes. The materials synthesized have a wide particle size distribution and most of the carbide particles observed had dimensions between 1 and 10 μm. Even though the carbothermal reduction process did not lead to a fully stoichiometric TiC, the CDC materials obtained after the high temperature chlorination process exhibit a classical XRD diffractograms and Raman spectra, characteristic of highly disordered micro-mesoporous carbon were obtained for all materials under study. Both the initial carbides and the final carbon material powders synthesized have micropores and mesopores. The DFT specific surface area values of the carbides vary between 152 and 274 m² g⁻¹. The synthesized CDCs have a noticeably high DFT specific surface area (up to 1710 m² g⁻¹), being higher than that usually obtained for chlorinated TiC-CDC. The addition of CNTs decreases the overall specific surface area, although the pore size distribution remains mostly unchanged. It is possible that the increase in mesoporosity (and DFT surface area) is caused non-stoichiometric structure of TiC and existence of TiO₂Cₓ inside raw carbide powder. Thus, the oxygen, left inside the raw complex material as titanium oxycarbide, is reacting with the formed carbon (forming CO₂ or CO) and as a result a more porous hierarchical structure will be created.

The energy-related properties of the supercapacitors based on 1 M (C₂H₅)₃CH₃NBF₄ solution in acetonitrile and the synthesized carbon materials as an electrode material were investigated using the cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge/discharge methods.

All sol-gel method TiC-CDC materials synthesized based EDLCs demonstrate practically ideal capacitive behavior at cell potential scan rate up to v ≤ 500 mV s⁻¹ and up to ΔE ≤ 3.4 V. Such high scan rates, while maintaining ideal capacitive behavior, have been previously only obtainable only via different methods involving very complicated templating methods of CDC materials. Cyclic voltammetry, impedance and constant current data indicate that even at such high potential scan rates (v ≤ 500 mV s⁻¹), there is no significant potential drop arising from the slow mass-transfer step in the porous CDC matrix. This is probably caused by the extra developed mesoporosity, because the sol-gel synthesis method provides additional pores into carbon powders in the range from 4 to 10 nm.

The highest integrated specific capacitance value C_{SCV} = 112 F g⁻¹ has been obtained for TiC-CDC at v = 10 mV s⁻¹. When the potential scan rate is increased up to v = 500 mV s⁻¹, this material still maintains a very high specific capacitance value C_{SCV} = 106 F g⁻¹.

The so-called round trip efficiency (RTE) for the cells has been calculated both as a ratio of charges released and accumulated (Q_{charge}/Q_{discharge}) and as a ratio of energy released and accumulated so-called energy efficiency during discharging and charging of the supercapacitors single cells, respectively. The calculated energy efficiency values for all synthesized carbon based systems vary within the range from 93.3% to 96.8% (at 1 A g⁻¹), while the calculated charge RTE values exceeded 99%, showing that synthesized powders are suitable for various energy storage applications including high power density electrodes for supercapacitors. The lower electrochemical performance of materials with CNTs can be explained by the specific surface area differences or that the pores or surfaces formed due to the inclusion of CNTs are not suitable for the formation of the electric double layer.

The Ragone plots for the supercapacitors have been calculated from constant power tests, demonstrating high gravimetric energy densities (20 Wh kg⁻¹) at very high power densities (200 kW kg⁻¹). Very high volumetric energy and power densities indicate that these materials can be used for different technological devices, including electrical double layer capacitors.

According to the combined durability testing method there is very slow decrease of cell capacitance (from 130 to 125 F g⁻¹) as well as shortening of charging/discharging times 5–10%. The Nyquist plots shape is practically independent of cycle numbers applied, however very small increase of series resistance 6–7% takes place. Also the capacitance decrease less than 15% during 2500 constant current charge /discharge cycles (total number) and 50 h (total holding) applied.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.03.081.

References


[94,95] or some pseudocapacitive nanocrystals [96] into the intermediate carbide or oxide to enhance either the electrochemical characteristics or other physicochemical parameters [97].


