



Electrochemical behavior of high performance on-chip porous carbon films for micro-supercapacitors applications in organic electrolytes



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H I G H L I G H T S

- On-chip CDC films were prepared with different pore sizes and thicknesses.
- Capacitance of 169 F cm⁻³ was achieved in either ACN- or PC-based electrolytes.
- EMI⁺ transport limitation occurred for thicker films in more viscous 2M EMIBF₄/PC.
- High energy density was obtained for 7 μm-thick CDC films in 2M EMIBF₄/ACN.

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Carbide derived carbons (CDCs) are promising materials for preparing integrated micro-supercapacitors, as on-chip CDC films are prepared via a process fully compatible with current silicon-based device technology. These films show good adherence on the substrate and high capacitance thanks to their unique nanoporous structure which can be fine-tuned by adjusting the synthesis parameters during chlorination of the metallic carbide precursor. The carbon porosity is mostly related to the synthesis temperature whereas the thickness of the films depends on the chlorination duration. Increasing the pore size allows the adsorption of large solvated ions from organic electrolytes and leads to higher energy densities. Here, we investigated the electrochemical behavior and performance of on-chip TiC-CDC in ionic liquid solvent mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) diluted in either acetonitrile or propylene carbonate via cyclic voltammetry and electrochemical impedance spectroscopy. Thin CDC films exhibited typical capacitive signature and achieved 169 F cm⁻³ in both electrolytes; 65% of the capacitance was still delivered at 1 V s⁻¹. While increasing the thickness of the films, EMI⁺ transport limitation was observed in more viscous PC-based electrolyte. Nevertheless, the energy density reached 90 μW h cm⁻² in 2M EMIBF₄/ACN, confirming the interest of these CDC films for micro-supercapacitors applications.

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1. Introduction

The myriad of portable electronic devices brings new needs in terms of mobility and autonomy, such as high performance miniaturized energy storage systems. While batteries are used for energy delivery, they still suffer from limited power capabilities and

cyclability, owing to the faradic nature of the electrochemical storage process.

Electrochemical double-layer capacitors (EDLCs), also called supercapacitors, store energy via reversible adsorption of ions from an electrolyte which is a fast non-faradic process, leading to high power densities and very long cycle life (more than 1,000,000 cycles) [1,2]. Therefore, this technology has already been used in broad range of applications in power electronics such as power buffer or memory back-up for toys, cameras, or mobile phones [1,3,4]. EDLCs are also used in transportation to recover braking energy in tramways, hybrid electric vehicles and buses [1,5].

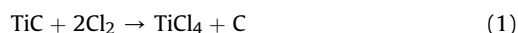
Among various active materials, carbide derived carbons (CDCs) have spawned much interest as they offer a unique pore size and pore size distribution control by selectively etching metal atoms from carbide powders, ceramics, felts and so on [6–13]. They demonstrated great performances as their pore diameter was adapted to the ion size, leading to important capacitance gains [14,15]. These materials can even compete with pseudocapacitive materials which deliver larger capacitance [16–19] but show a decrease in power capabilities because of the faradic reactions kinetics [18,20].

CDC powders have been widely studied in tetraalkylammonium tetrafluoroborate based electrolytes in acetonitrile (ACN) [8,21,22], propylene carbonate (PC) or γ -butyrolactone [23], as well as in ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate [24–26] and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [27]. Unfortunately, mixing high specific surface area carbon powders with a binder to prepare film electrodes does not fit with the requirements of the semiconductor industry, where thickness control and good adherence on silicon chips are needed. To overcome this technological barrier, CDC began to be synthesized from the chlorination of metal carbide films sputtered by physical vapor deposition technique [28], allowing the direct integration of CDC films on silicon wafers to prepare micro-supercapacitors [29,30]. These on-chip CDC films showed very good adherence with rubber-like mechanical properties and delivered very high capacitance of 410 F cm^{-3} in $1 \text{ M H}_2\text{SO}_4$ and 160 F cm^{-3} in 2 M EMIBF_4 in ACN [31]. However, so far, no studies have addressed the influence of CDC films structure and texture on the electrochemical behavior in various electrolytes. This work investigates the electrochemical behavior and performance of on-chip micrometer-thick TiC-CDC in EMIBF₄ diluted in either acetonitrile or propylene carbonate for micro-supercapacitors applications.

2. Experimental

2.1. Material preparation

TiC films were deposited by using a non-reactive direct current magnetron sputtering technique (DC-MS) on Si/SiO₂ wafers. A TiC target (99.5%, 10 cm diameter, 6 mm thick) was sputtered under argon atmosphere in the DP 650 sputtering equipment (Alliance Concept) under 0.01 mbar at 750 °C as described in previous work [31]. The power density was kept at 2 W cm^{-2} during the sputtering deposition. The thickness of the sputtered TiC thin films is controlled by the deposition time. Then the deposited TiC was placed in a furnace under argon purge. When the desired temperature was reached, the titanium carbide was converted to TiC-CDC by reacting with chlorine gas as described below (1):



The chlorination time was carefully controlled to perform partial chlorination and obtain a CDC film strongly bonded to a residual

conductive TiC layer underneath [31].

Chlorination temperatures of 450 °C and 700 °C were selected to prepare CDC films with different structure (pore size and pore size distribution). On-chip CDC films of more than 1 cm^2 were obtained (Fig. 1A). The structure of the TiC precursor is preserved after conversion into CDC for both 450 °C (Fig. 1B and C) and 700 °C (Fig. 1D and E) chlorination temperatures, with continuous columnar structure [31]. Cooling down was done under argon and further annealing was performed at 600 °C under H₂ atmosphere to remove residual chlorine species trapped into the nanopores [10].

2.2. Structural and electrochemical characterization

Raman spectra of the chlorinated CDC films were recorded using a Raman spectrometer LabRAM HR (Horiba Yvon-Joblin, 514 nm wavelength).

Gas sorption experiments were achieved on self-supported CDC films fully chlorinated at the desired temperatures and placed in a BELSORP-mini II (BEL, Japan) apparatus. The Ar and CO₂ adsorption isotherms were used to estimate the Brunauer-Emmett-Teller (BET) surfaces and the pore size distributions.

The electrochemical characterizations of the Si/SiO₂/TiC/CDC were conducted using a Biologic VMP3 Potentiostat in 2M EMIBF₄ either in acetonitrile or propylene carbonate (conductivities of 60 mS cm^{-1} and 17 mS cm^{-1} in ACN and PC, respectively) [32] in a three-electrode configuration. All experiments were carried out at room temperature under Ar atmosphere (O₂ and H₂O contents lower than 0.1 ppm). A silver wire was used as quasi-reference and a Pt foil as counter electrode. Electrochemical impedance spectroscopy (EIS) measurements were conducted on the freshly assembled cells by applying a 5.0 mV_{RMS} sinusoidal signal amplitude from 100 kHz to 10 mHz at the open circuit potential, and cyclic voltammetry was performed at several scan rates.

The electrolyte viscosities were measured with a MCR 301 Rheometer (ANTON PAAR, Austria) with a shear rate moving from 10 to 1000 s⁻¹. Each measurement was repeated twice.

3. Results and discussion

3.1. Chlorination temperature influence

CDC film properties can be tuned starting from the same TiC thin film by changing the chlorination parameters such as temperature and time. The chlorination temperature affects the structural and textural properties [6,14], modulating the pore size distribution, BET surface area, disorder and mechanical strength, while the chlorination time mostly controls the film thickness [31]. Fig. 2A shows the Raman spectra of 450 °C and 700 °C partially chlorinated on-chip TiC-CDC samples. Whereas perfectly ordered graphite usually exhibits only one G-peak at 1580 cm^{-1} , corresponding to in-plane stretching, the second D-peak at 1350 cm^{-1} is associated with disordered carbons. Here, D-band and G-band are clearly visible around 1340 cm^{-1} and 1590 cm^{-1} , respectively, revealing the carbon is only partially graphitized for both 450 °C and 700 °C chlorination temperatures. No peaks are observed at low Raman shifts, confirming that titanium carbide layer was successfully converted into CDC [33]. Furthermore, as studied for SiC-CDC and Mo₂C-CDC [34], the deconvolution of the pics using a Gaussian-Lorentzian function evidences that the I_D/I_G ratio changes while increasing the chlorination temperature, from 1.4 at 450 °C to 1.7 at 700 °C, with a noticeable shift of the G-peak from 1585 cm^{-1} to 1594 cm^{-1} . This was also described for Ti₃SiC₂ ternary carbides [6]. As proposed by Ferrari and Robertson [35], the I_D/I_G ratio is proportional to the square of the in-plane correlation length L_a for more disordered carbons; aside, the

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