Capacitance of KOH activated carbide-derived carbons†

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Chemical activation of CDC leads to capacitance values in an organic electrolyte as high as 180 F/g, 30% larger than those of as-produced samples, due to the surface area and microporosity development occurring as a consequence of the activation.

Electrochemical capacitors (EC) are the most efficient electrical energy storage devices, and thus are of interest for applications ranging from hybrid electric vehicles to portable electronics. Because of the electrostatic charge storage at the electrolyte/electrode interface, they have a power density higher than that of batteries and their cyclability is theoretically infinite. However, increasing the energy stored by these devices remains a challenge.

Extensive studies have been performed in the past few years to understand the relation between the carbon properties and the capacitance arising from the electrical double layer. Porosity was found to play a major role along with the presence of functional groups. A significant increase in the capacitance was obtained for carbons with pore size smaller than the solvated ion size in organic electrolytes. It was attributed to a distortion and partial desolvation of ions minimizing the distance between the ion and the pore wall as well as increasing the number of ions per unit of pore volume.

Different routes have been explored in order to increase the capacitance in organic electrolytes, via the modified carbide synthesis, chemical or physical activation, and nitrogen doping. However, tuning the pore size is the most efficient way to improve the energy density. An example is the high capacitance obtained on carbide-derived carbon (CDC) produced from TiC. The narrow pore size distribution of CDCs can be controlled by modifying the synthesis conditions. Since the transformation of carbide to carbon is conformal, the total pore volume of 55% in CDC is determined by the number of carbon atoms per unit of carbide volume.

In the past few years, chemical activation was investigated to study the development of the porosity of carbon materials produced from natural and synthetic precursors. In this communication, we report the influence of a chemical activation treatment on CDC properties, and its beneficial effect on the electrochemical performance of EDLC electrodes.

CDCs have been produced from titanium carbide at different chlorination temperatures (from 400–1000 °C) and post-treated under H2. The experimental setup and process have been detailed elsewhere. KOH activation has been performed using a KOH/precursor ratio of 3/1 (w/w). For comparison, other KOH activated carbon materials have been prepared from anthracite or phenolic resin precursor using KOH/precursor ratios ranging from 1/1 to 3/1 using the experimental procedure described in ref. 12.

Porosity analysis was carried out with a Quantachrome 6-B apparatus. N2 sorption at 77 K and CO2 sorption at 273 K were performed from relative pressure P/P0 of 10–4 to 1 for nitrogen and from 0.0288 to 1 for CO2. The surface area was calculated from the BET model using N2 isotherm. Total micropore volume (pores < 2 nm) was determined with N2 isotherms applying the Dubinin-Radushkevich equation, while narrow micropore volumes (<0.7 nm) were measured applying the Dubinin-Radushkevich equation to CO2 sorption data. A two-electrode cell has been assembled in a glove box under controlled atmosphere. Electrodes were constituted of painted Aluminium current collector and active material based on 94 wt% of carbons and 6 wt% of PTFE with a constant mass of 50 mg. Cell assembly and process have been described elsewhere. The electrolyte used is a dried NEt4BF4 salt dissolved in acetonitrile (1.5 M). Galvanostatic cycling and electrochemical impedance spectroscopy measurements were performed to compare the capacitive behaviour of the cells. Table S1 and S2 (ESI) summarize the results obtained from gas sorption and electrochemical measurements of the cells assembled with CDC and microporous KOH activated carbons, respectively.

Independently of the type and origin of the carbon precursor used (CDC is a member of the large carbon family), KOH activation occurs through the following reaction:

$$6\text{KO} + 2\text{C} \leftrightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3$$

However, the difficulty of the activation reaction, the yields of the process as well as the resulting porosity development depend very much on the structural order of the precursor used. As a result, the activation process will vary as a function of the CDC synthesis temperature.

The alkaline hydroxide activation of the TiC-derived carbons has never been reported in the literature. In order to understand how their activation takes place, it is important to focus on the type of CDC, temperature and type of gas used. In the present study, CDCs precursors (from TiC) were prepared using chlorination temperatures ranging from 400 to 1000 °C.

The results of KOH activation show that the porosity of CDC depends on the synthesis temperature. The porosity measured by N2 and CO2 sorption (see ESI) dramatically...
increases as shown in Fig. 1. The $N_2$ isotherms of as-produced and activated CDC are type I suggesting their microporous character (Fig. 1a and b). The specific surface area (SSA) increases for all CDCs, almost twice as large as the pristine ones (Fig. 1c). Both micropore volume ($<2$ nm) and volume of pores smaller than the ion size ($<0.7$ nm) increase with the chlorination temperature and start decreasing at $800^\circ C$, proving the initial porosity plays an important role in the activation process (Fig. 1d). Those results demonstrate that the lower the chlorination temperature, the more efficient the activation is. These results are in agreement with results obtained for the activation of other heat-treated carbon precursors$^{12,17}$ and can be explained as a result of the structural order of the precursor. The CDC-precursors are essentially amorphous carbon materials whose structural order increases with the increase in the synthesis temperature.$^{18}$ Literature has shown that alkaline hydroxide activation is more efficient for materials with moderate-to-low structural order than for graphitic materials.$^{12,17}$ However, since CDC samples have been synthesized at $400^\circ C$ or above, the detrimental effect of increasing the synthesis temperature is more likely seen for the $800$ and $1000^\circ C$ samples.

Pores larger than $2$ nm, not present in the pristine samples, are formed during the activation process as presented in Fig. 1 proving that CDCs undergo the same steps observed during activation of other carbons with the enlargement of micropores into larger pores and reformation of new small pores.$^{12}$

Galvanostatic cycling measurements performed between $0$ and $2.3$ V reveal a linear charge-discharge behaviour at any currents varying from $5$ to $400$ mA. This characteristic suggests that the capacitance mainly comes from the double layer formation and the pseudocapacitance arising from oxygenated functional groups created during activation is negligible. At a current of $20$ mA, very high capacitance values between $150$–$180$ F g$^{-1}$ were measured after activation (Fig. 2); those values are much higher than the one observed for other activated carbons in the same organic electrolyte. $^{6,19}$ The maximum gravimetric capacitance was reached for the CDC synthesized at $600^\circ C$ before and after activation due to the maximum fraction of pores below $0.7$ nm present in those samples. The average pore size increase obtained for the activated CDC, which could lead to a capacitance decrease according to previous studies,$^{5,6}$ is not observed. The increase in the BET SSA, pore volume and micropore volume compensates the pore size effect. Microporous carbons produced from anthracite and phenolic resin activated under KOH$^{12}$ have been tested and followed the same trend: the highest gravimetric capacitance was measured for the sample having the highest SSA and micropore volume (see ESI). Moreover, the capacitance saturation described by Barbieri et al.$^{20}$ for carbons exhibiting surface area above $1500$–$1600$ m$^2$ g$^{-1}$ is not observed in this case, proving that the electrode structure plays an important role.

Fig. 3 represents the Nyquist plots of cells assembled with KOH activated CDC tested between $1$ kHz and $10$ mHz at a fully discharged state. No high frequency RC loops are

Fig. 1 $N_2$ adsorption isotherms for CDC before and after KOH activation (a) and (b); change of BET SSA (c); pore volumes of CDC before (solid line) and after (dash line) KOH activation (d).
noticeable in the Nyquist plots of cells using activated CDC (Fig. 3b) proving a good contact throughout the electrode; the same behaviour was obtained in the case of as-produced CDC. 5 The internal resistance measured at 1 kHz reveals values between 1 and 1.5 Ω cm², increasing when the temperature was decreasing from 1000 °C to 400 °C. Those values are slightly higher than the one measured on the as-produced CDC. The resistance decrease observed at higher temperature is partially due to the increase in CDC electrical conductivity.

The normalized capacitance vs. the average pore size of CDC before/after KOH activation is plotted in Fig. 4. A decrease of the normalized capacitance is observed when increasing the average pore size and confirms the mechanism of charge storage of the ions in the double layer. Subnanometre pores lead to a more efficient adsorption of ions. 5 However, high capacitance can be reached by developing a large volume of micropores, even if the porosity is not exploited in the most efficient way. An adequate subnanometre pore/micropore volume ratio associated to a high total pore volume and high SSA allows an increase in the capacitance.

In summary, this study reveals that subnanometre pores smaller than the solvated ion size remain the most efficient, as shown in Fig. 4, to improve the capacitance. However, the gravimetric capacitance is enhanced by 30% when the surface area and volume of pores above the solvated ion size increases proving the efficiency of the activation process. The surface area and volume of pores between 1 and 2 nm increase compensates the subnanometre pore volume fall-off of the KOH-activated CDC.

Chemical activation of CDC is a powerful tool to improve electrical double layer performances due to an increase of volume of small pores <2 nm. Outstanding capacitances have been obtained with carbons exhibiting pore sizes larger than 0.7 nm, SSA around 2000 m² g⁻¹ and pore volume below 1 cm³ g⁻¹. The additional capacitance coming from 1–2 nm micropores leads to a dramatic gravimetric capacitance improvement. The capacitance values reached with CDC chemically activated are very attractive to develop high energy EDLC devices in organic electrolyte. Taking into the account that chlorination of carbides has been used for decades in large-volume synthesis of metal chlorides, 21 in which carbon residue was discarded, this is a promising process for manufacturing inexpensive, high-capacitance carbon for ECs and other applications.

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References