Nuclear Magnetic Resonance Study of Adsorption of Electrolyte Ions on

Carbide-derived Carbon

Electronic Supplementary Information

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1. Structure of Carbide-derived Carbon

All carbide-derived carbon (CDC) samples were derived from a powder material. In the case of conventional TiC-CDC, commercial powder with a small particle size (around 2 μ m) was used, whereas Ti¹³C-CDC was derived from particles with a broader size distribution and a larger average particle size. Scanning electron microscope (SEM) images of TiC-CDC-1000 and Ti¹³C are shown in Figure S1.



Figure S1 SEM images of TiC-CDC-1000 (a, b) and of the sample material, Ti¹³C, prior to chlorine treatment (c, d).

2. Porosity Analysis of Carbide-Derived Carbon

Nitrogen sorption analysis was carried out using Quantachrome Instruments (U.S.A.) Autosorb system at -196 °C. Pore size distributions (PSDs) and pore volumes were determined using the quenched solid density functional theory (QSDFT) method¹ on the desorption branch of the isotherms. All samples are predominantly microporous with a small volume fraction of the total

pore volume associated with pores larger than 2 nm. The cut-off of the nitrogen gas sorption analysis is around 30 nm so that no interparticle pores between the CDC grains are considered. The results of the porosity analysis are provided in Table S1 and Figure S2.

Sample Name	BET SSA [†]	$\begin{array}{c} \mathbf{QSDFT}\\ \mathbf{SSA}^+ \end{array}$	Total pore volume ⁺	Micropore volume ⁺	Mesopore volume⁺	Pore size average [*]
	$m^{2} \cdot g^{-1}$	$m^{2} \cdot g^{-1}$	$cm^3 \cdot g^{-1}$	%	%	nm
TiC-CDC-600	1458	1352	0.581	92.9	7.1	0.815
TiC-CDC-800	1702	1417	0.701	92.4	7.6	0.906
TiC-CDC-1000	1723	1570	0.767	85.9	14.2	0.932
Ti ¹³ C-CDC-1000	1685	1476	0.728	90.1	9.9	0.998

Table S1 Porosity analysis using N2 gas sorption @ 77 K.

[†] Specific surface area after Brunauer, Emmett, and Teller (BET SSA)² was calculated in the linear regime in the relative pressure range from 0.05 to 0.20 P/P₀.

⁺ calculated from the cumulative pore volume employing Quenched Solid Density Functional Theory, QSDFT.





Figure S2 Nitrogen sorption isotherms (a) and pore size distribution plots (b) of TiC-CDC and Ti¹³C-CDC.

3. Structure of a TiC-CDC-1000 Film

An SEM image of a TiC-CDC-1000 film is shown in Figure S3. Spaces between the carbon particles accommodate reservoirs of electrolyte giving rise to ex-pore signals in NMR spectra.



Figure S3 SEM image of a TiC-CDC-1000 film. Spaces between carbon particles may accommodate reservoirs of electrolyte.

4. Fits of Spectra in the Main Text

Fits were performed using dmfit software.³ As described in the main text, a Gaussian line shape was used to fit the in-pore environment, whilst for the ex-pore environment (and free electrolyte features) the Gaussian/Lorentzian ratio was allowed to vary. The ¹¹B fit is shown in Figure S4 (a), three peaks were used in the fitting. The ¹⁹F fit is shown in Figure S4 (b), an additional peak was used to fit a free electrolyte feature present in this sample.



Figure S4 Fits of ¹¹B (a) and ¹⁹F (b) spectra referred to in the main text. Spectra are of bag samples containing TiC-CDC-1000 (6.0 mg) and NEt₄BF₄/ACN electrolyte (10.0 μ L), although different samples were studied for each NMR nucleus.

5. Calculation of the Area Containing One Anion

Since a known volume of electrolyte is added to each sample, the total number of BF_4 anions in the plastic bag, *N*, can be calculated by:

 $N = cVN_a$ [Equation 1]

where *c* is the electrolyte concentration (mol·L⁻¹), *V* is the loading volume (L) and N_a is Avogadro's number. The fraction of ions that are in-pore, *f*, is obtained from fitting of the NMR spectra (see above). A single Gaussian peak was used to fit the in-pore feature, whilst for the expore feature and any free electrolyte features, the Gaussian/Lorentzian ratio was allowed to vary. We obtain the number of in-pore anions, $N_{in-pore}$, by:

$$N_{in-pore} = fN$$
 [Equation 2]

Assuming these anions are evenly distributed in a monolayer on a planar carbon surface with specific surface area A (m²·g⁻¹) and mass m (g), we can find the area per anion, κ (m²) by:

$$\kappa = \frac{mA}{N_{in-pore}} = \frac{mA}{fN} = \frac{mA}{fcVN_a}$$
 [Equation 3]

A theoretical lower limit for this value can be calculated by considering a close packed square lattice of solvated anions and cations. Figure S5 illustrates this arrangement.



Figure S5 Close packed square lattice of solvated anions (white) and cations (light blue).

The unit cell shown contains one anion. It follows from simple geometry that the minimum surface area per anion (assuming no desolvation), κ_{lim} , is given by:

$$\kappa_{\rm lim} = \frac{(d_{anion} + d_{cation})^2}{2}$$
 [Equation 4]

where d_{anion} and d_{cation} are the sizes of the solvated ions. Taking values⁴ of 1.16 and 1.30 nm for d_{anion} and d_{cation} respectively, we find $\kappa_{lim} = 3.0 \text{ nm}^2$.

6. ¹⁹F Sample Orientation Study

 $^{19}\mathrm{F}$ static NMR spectra of a sample in a bag containing TiC-CDC-1000 (6.0 mg) and NEt₄BF₄/ACN electrolyte (10.0 $\mu\mathrm{L}$), in the horizontal and vertical orientations, are shown in Figure S6.



Figure S6 Static ¹⁹F (7.05 T) NMR spectra of a piece of TiC-CDC-1000 film soaked with 10.0 μ L of NEt₄BF₄/ACN electrolyte, in the horizontal and vertical orientations. NMR parameters were as described in the main text.

Sample orientation has a large effect on the form of the NMR spectrum, the effects very similar to those seen in ¹¹B spectra (see Figure 3 in the main text) and are again attributed to bulk magnetic susceptibility effects. The in- and ex-pore features shift by ~ 9 and 7.8 ppm respectively on changing the sample orientation. Resolution of the features is better in the vertical orientation.

7. ¹⁹F Adsorption Study in the Horizontal Orientation

The spectra presented in Figure 4 in the main text were also recorded in the horizontal orientation, shown in Figure S7. On loading the in-pore feature is observed first at low frequencies. Addition of further electrolyte causes this feature to grow and then saturate, whilst the ex-pore feature then grows considerably. The in-pore feature shifts to higher frequencies on the addition of more electrolyte.



Figure S7 Static ¹⁹F (7.05 T) NMR spectra of TiC-CDC-1000 film pieces soaked with different volumes of NEt_4BF_4/ACN electrolyte, acquired in the horizontal orientation. NMR parameters were as described in the main text.

8. ¹H Adsorption Study

A ¹H NMR adsorption study was carried out on TiC-CDC-1000 to probe the adsorption of the NEt₄ cations. Figure S8 shows the static ¹H spectra of samples in bags containing pieces of TiC-CDC-1000 film (6.0 mg) soaked with different volumes of NEt₄BF₄/dACN electrolyte, acquired in the vertical orientation. The spectrum of an empty piece of the plastic bag used to contain samples is also shown.



Figure S8 Static ¹H (7.05 T) NMR spectra of TiC-CDC-1000 film pieces soaked with different volumes of NEt₄BF₄/dACN electrolyte, acquired in the vertical orientation. Spectra are complicated by the presence of the plastic bag signal shown at the top of the figure. A spin-echo pulse sequence ($\tau = 4$ ms) was used, with each spectrum the result of coadding 32 transients, separated by a recycle interval of 3 s.

The spectra show in- and ex-pore environments for the NEt₄ cations, and are in qualitative agreement with studies of the BF₄ anions (Figures 1 and 4 in the main text). However, analysis of the spectra is complicated by the presence of the ¹H signal from the plastic bag (Figure S8, top) used to contain the sample. This background peak falls directly on top of the ex-pore features and is not easily subtracted from spectra since the exact amount of plastic bag used for each sample varies. Use of a relatively long spin echo τ delay (4 ms here) helps resolve the in-pore peak, but intensity is lost due to transverse T_2 relaxation effects. Experiments were also carried out in the horizontal orientation (not shown), but poorer resolution of features was observed.

9. Cross Polarisation Pulse Sequence

The pulse sequence for the ${}^{13}C \rightarrow {}^{1}H$ cross polarisation experiment is shown in Figure S9. The ${}^{1}H$ contact pulse power is ramped linearly from 50% to 100% of its chosen value.



Figure S9 Pulse sequence (timing diagram) for the cross polarisation experiment.

References

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