

Nuclear Magnetic Resonance Study of Ion Adsorption on Titanium Carbide-derived Carbons

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Supercapacitors are high power energy storage devices with essentially unlimited cycle lives.¹ Porous carbons are popular supercapacitor electrode materials as they have high surface areas for charge storage by ion adsorption. In particular, titanium carbide-derived carbon (TiC-CDC) has recently attracted great attention as it has a pore size that is tuneable on the nanoscale.² Control of the carbon pore size has shown that the highest capacitances are achieved at subnanometre pore sizes.^{3,4} In spite of recent experimental and theoretical advances, the charge storage mechanism in porous carbons is not well understood.⁵ New characterization methods must be developed to probe the structure of the electrode-electrolyte interface, and how this changes during charging.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for studying electrochemical interfaces. It is element selective, and the resonance frequencies observed are sensitive to the local environments of the nuclei. NMR spectroscopy has been used to study the structure of the electrode-electrolyte interface in TiC-CDC.⁶ NMR experiments on carbons soaked with different volumes of

NEt₄BF₄/acetonitrile electrolyte reveal two main ion environments (Figure 1). In-pore ions are adsorbed to the carbon inside the pores, whilst ex-pore ions (observed at higher frequencies) are not adsorbed and are in large reservoirs of electrolyte between carbon particles. Experiments performed on TiC-CDCs with different pore sizes revealed that the number of ions adsorbed at zero potential decreases with pore size. This different pore-wetting behavior is expected to have a significant effect on the charging mechanism. A ¹³C - ¹H inverse cross polarisation experiment enabled magnetisation transfer from the carbon architecture to the adsorbed species, allowing their selective observation (Figure 1).

To study working supercapacitor devices, *in situ* NMR methods⁷ have been developed, where NMR spectra are acquired during charge and discharge. Shifts of the in-pore resonance are observed as the applied potential is varied, along with changes in intensity of peaks from the different environments. The effect of TiC-CDC pore size on the charging behavior is currently being investigated.

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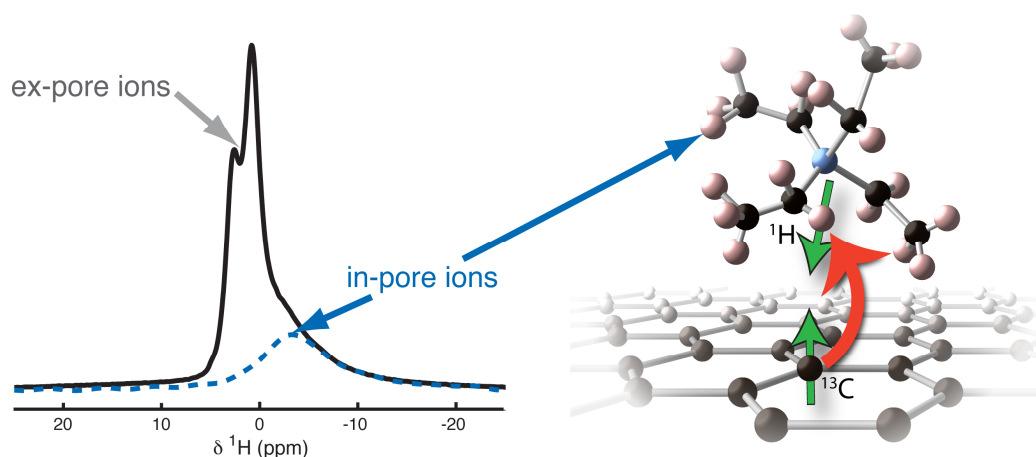


Figure 1: Left panel: direct (black) and ¹³C - ¹H inverse cross polarisation (blue, dashed) spectra of a carbide-derived carbon soaked with electrolyte. Right panel: Schematic illustrating transfer in the inverse cross polarisation experiment.