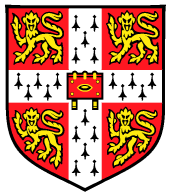


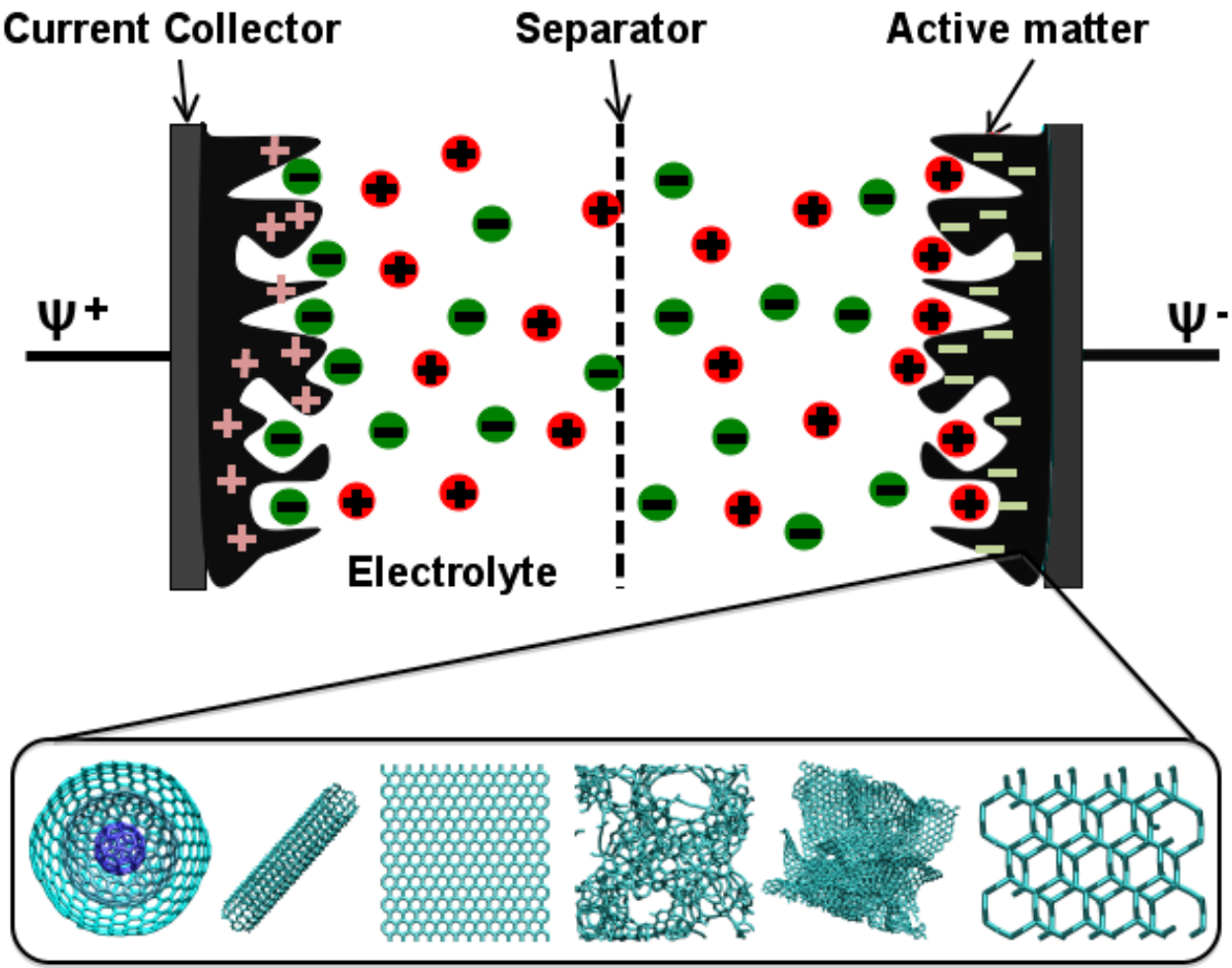
UNIVERSITY OF CAMBRIDGE

NMR study of the electrode/electrolyte interface in supercapacitors

Céline Merlet, Alexander C. Forse, John M. Griffin, Daan Frenkel and Clare P. Grey

October 3, 2015

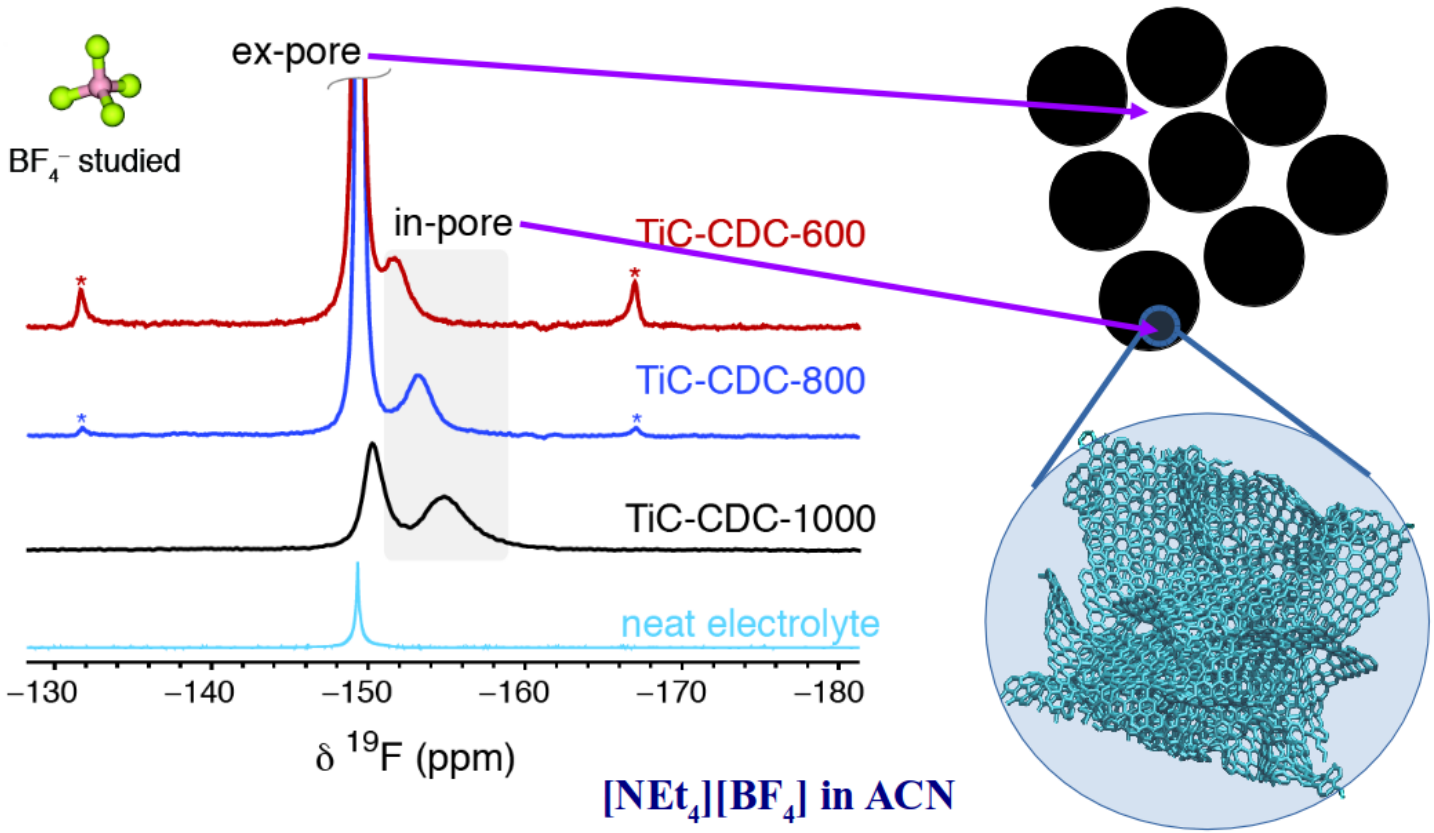
Electrochemical double layer capacitor: principle



- Ion adsorption: no redox reaction
- Characterisation of the porosity? the ion adsorption?

NMR experiments on porous carbons

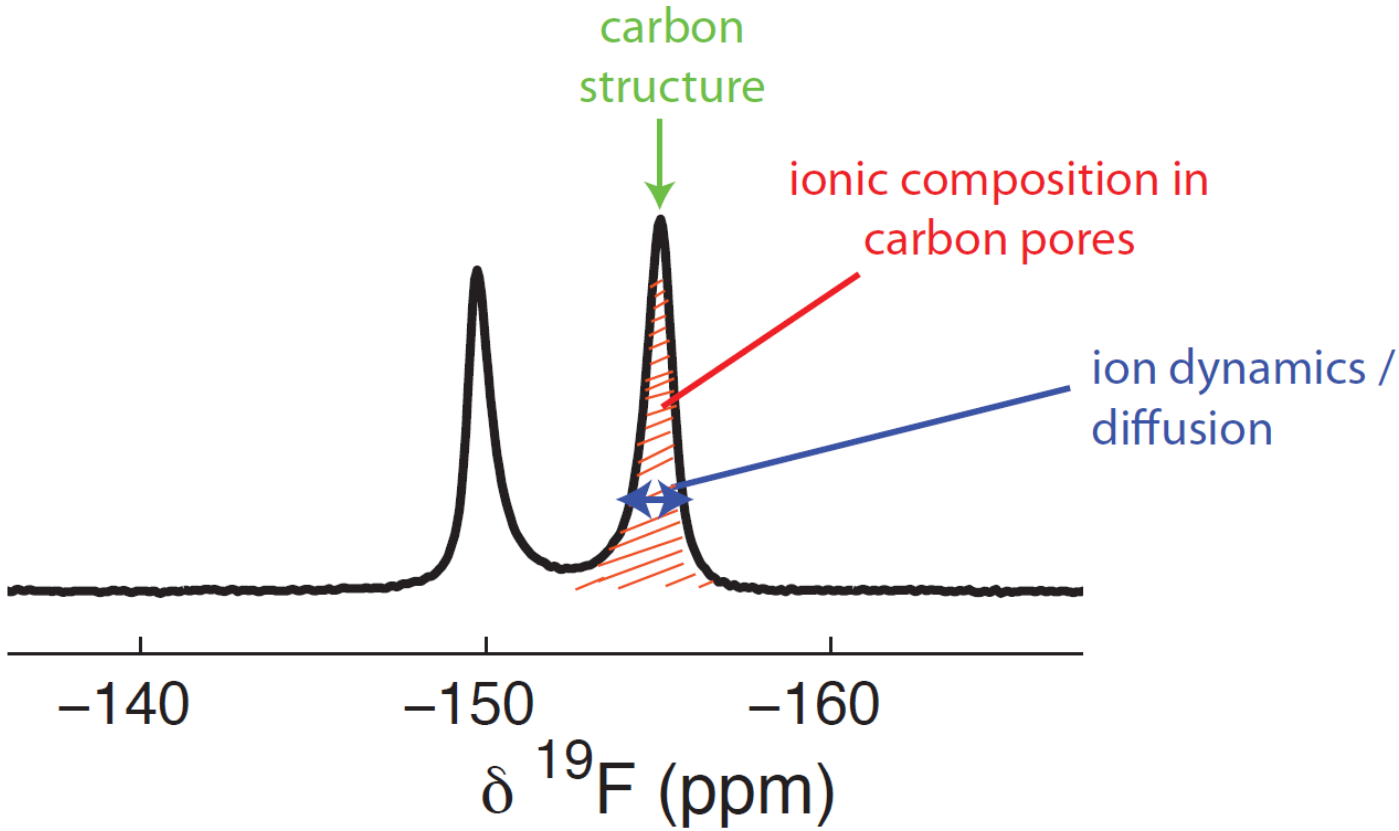
- Probe the local environment of chosen nuclei



- Always two peaks: ex-pore and in-pore
- Position of the in-pore peak depends on the carbon structure.

A. C. FORSE *et al.*, *J. Phys. Chem. C*, **118**, 7508 (2014)

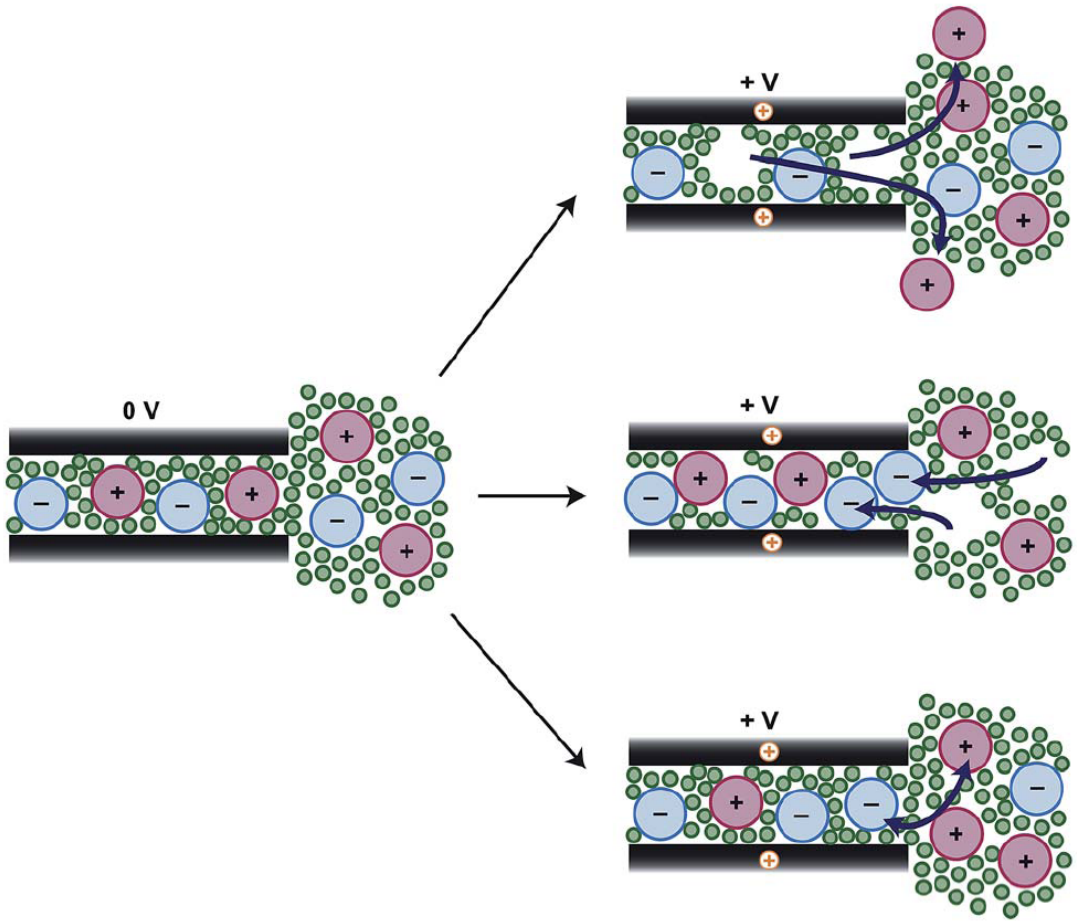
NMR peak: 3 sources of information



- Quantity of adsorbed ions from area under the peak
- Information on the dynamics from the linewidth
- Combined experimental and theoretical study to learn about the carbon structure

Insights into the mechanism of charge

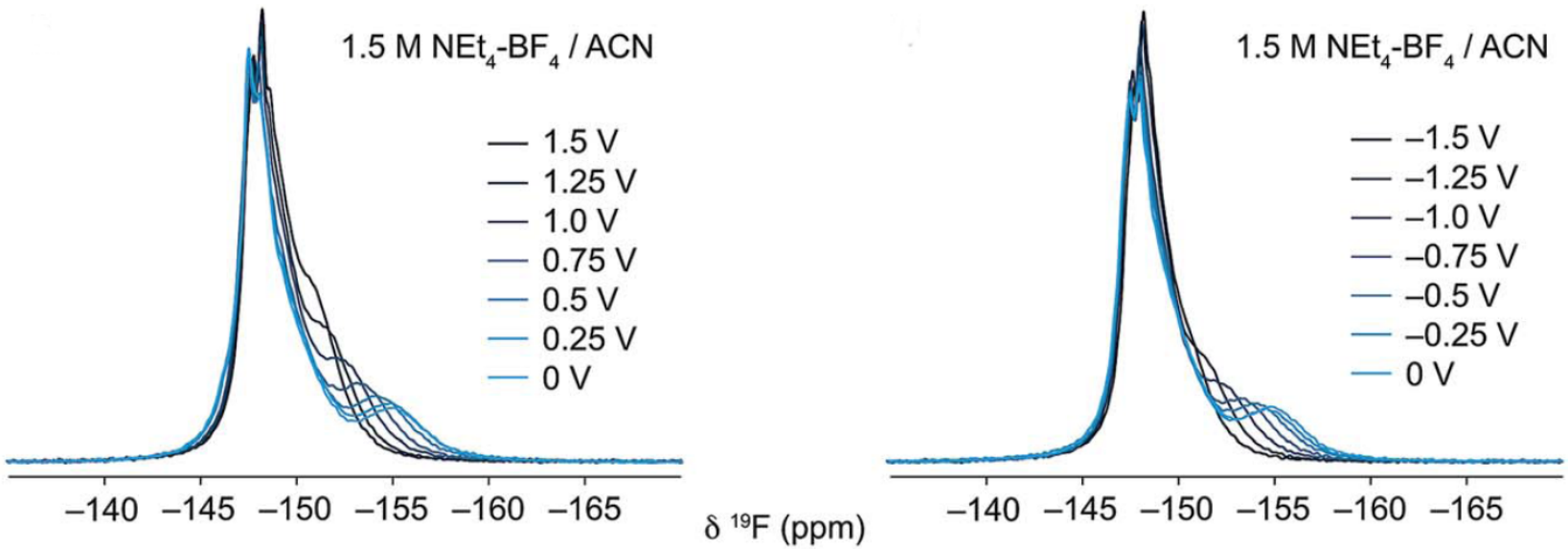
- Different possible charge storage mechanisms



J. M. GRIFFIN *et al.*, *Faraday Discuss.*, **176**, 49 (2015)

In situ NMR (YP-50F and $[NEt_4][BF_4]$ in ACN, 1.5 M)

- Focus on the BF_4^- anion

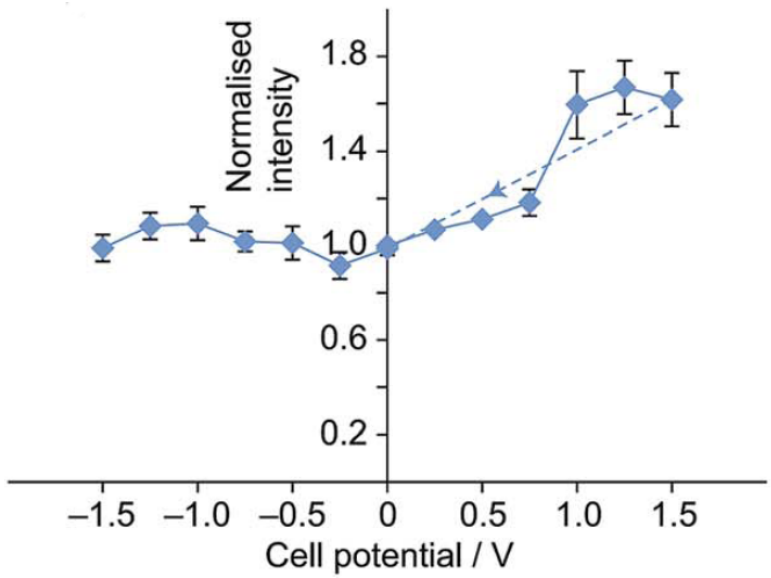


- The chemical shift depends on the applied potential.
- The normalised intensity of the peaks is proportionnal to the quantity of ions.

J. M. GRIFFIN *et al.*, *Faraday Discuss.*, **176**, 49 (2015)

In situ NMR (YP-50F and $[NEt_4][BF_4]$ in ACN, 1.5 M)

- Focus on the BF_4^- anion

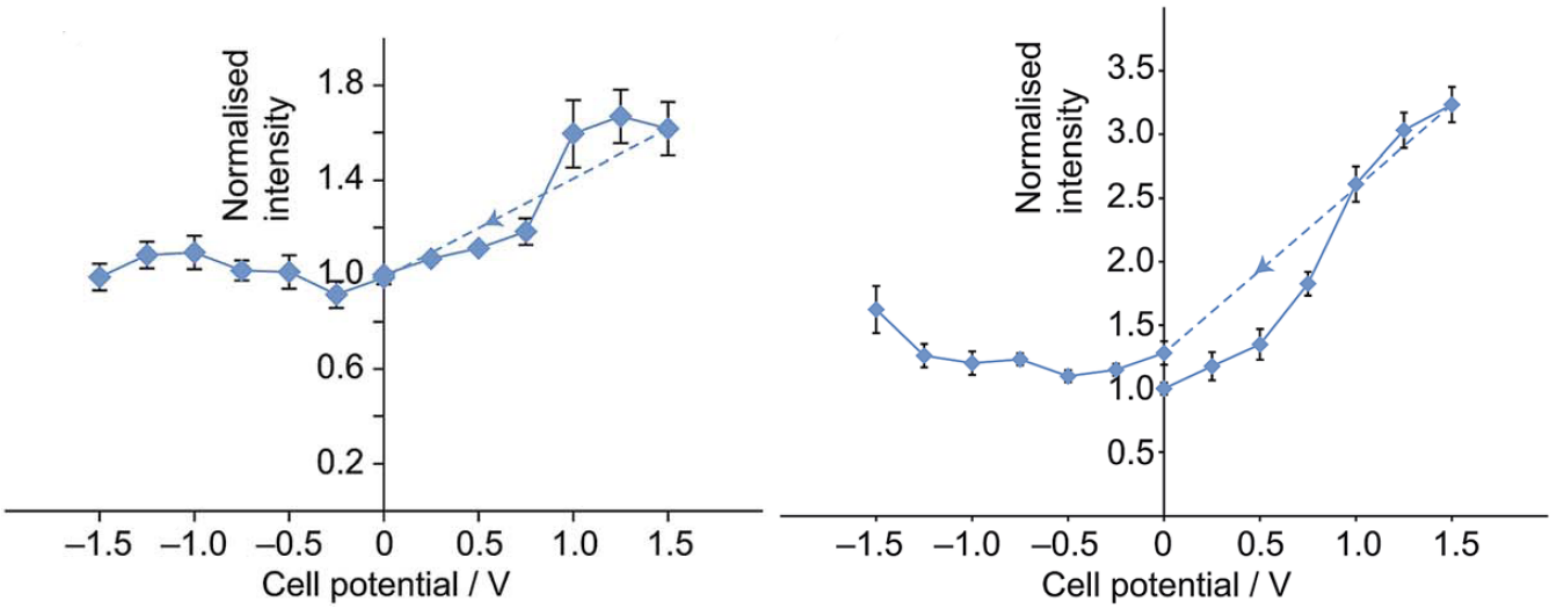


- Negative electrode: quantity of adsorbed anions almost constant.
- Positive electrode: quantity of adsorbed anions increases.

J. M. GRIFFIN *et al.*, *Faraday Discuss.*, **176**, 49 (2015)

In situ NMR (YP-50F and $[NEt_4][BF_4]$ in ACN)

- Effect of concentration: 1.5 M (left), 0.5 M (right)

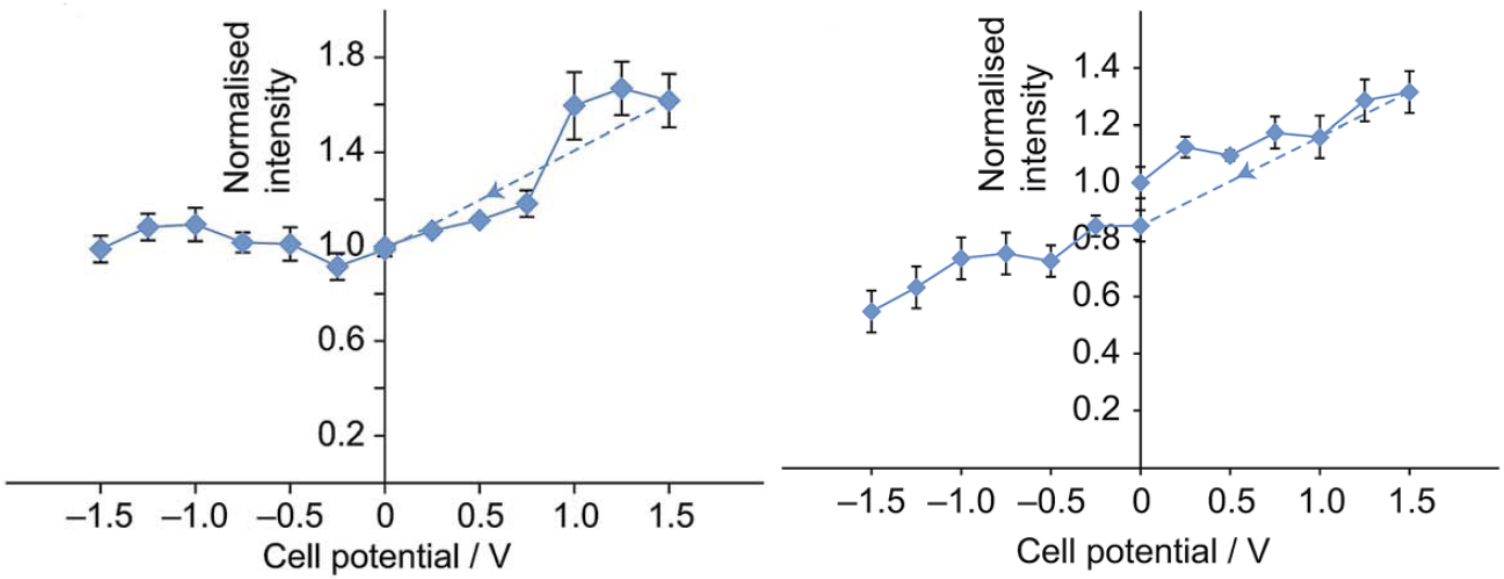


- Negative electrode: quantity of adsorbed anions almost constant.
- Positive electrode: quantity of adsorbed anions increases more when concentration is reduced.

J. M. GRIFFIN *et al.*, *Faraday Discuss.*, **176**, 49 (2015)

In situ NMR (YP-50F and ammonium salt in ACN, 1.5 M)

- Effect of cation size: NEt_4^+ (left), NBu_4^+ (right)

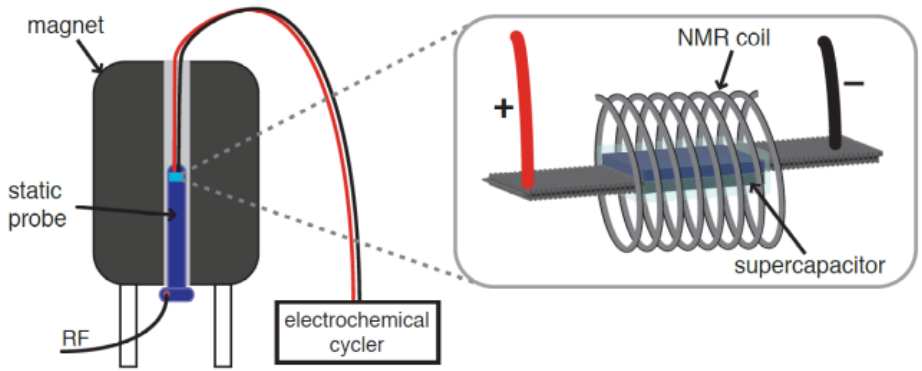


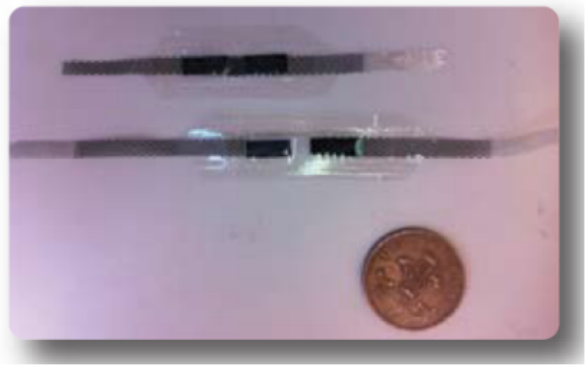
- Anions expulsed from negative electrode → steric effects
- Different charge mechanisms for different electrolytes
- What about ionic liquids?

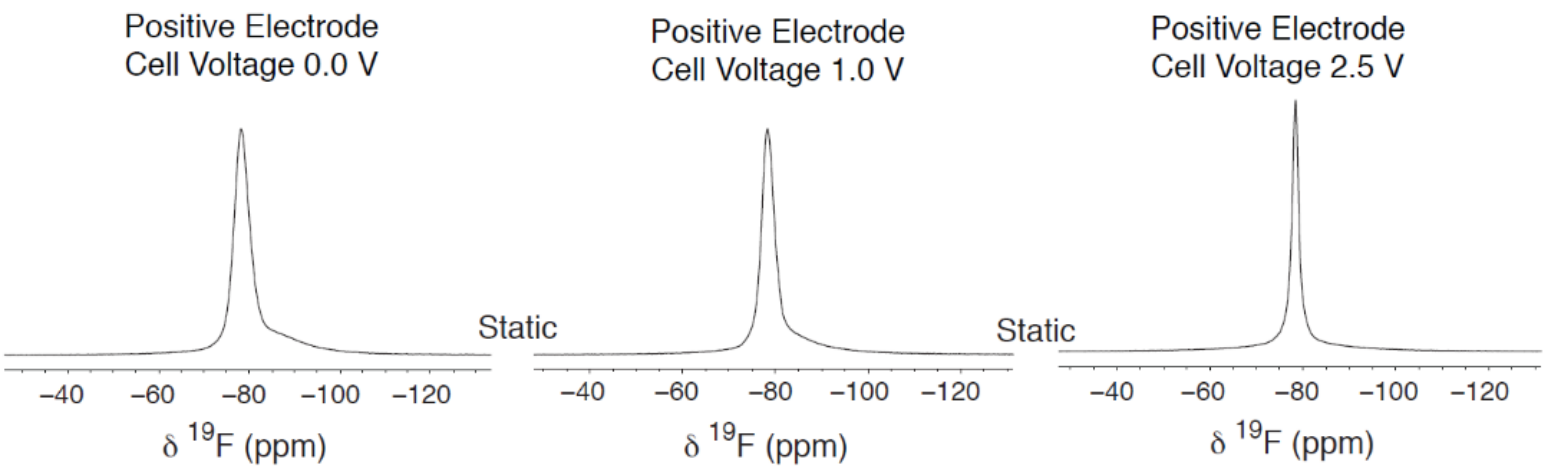
J. M. GRIFFIN *et al.*, *Faraday Discuss.*, **176**, 49 (2015)

In situ NMR for ionic liquids?

- YP-50F and [Pyr_{13}][TFSI]



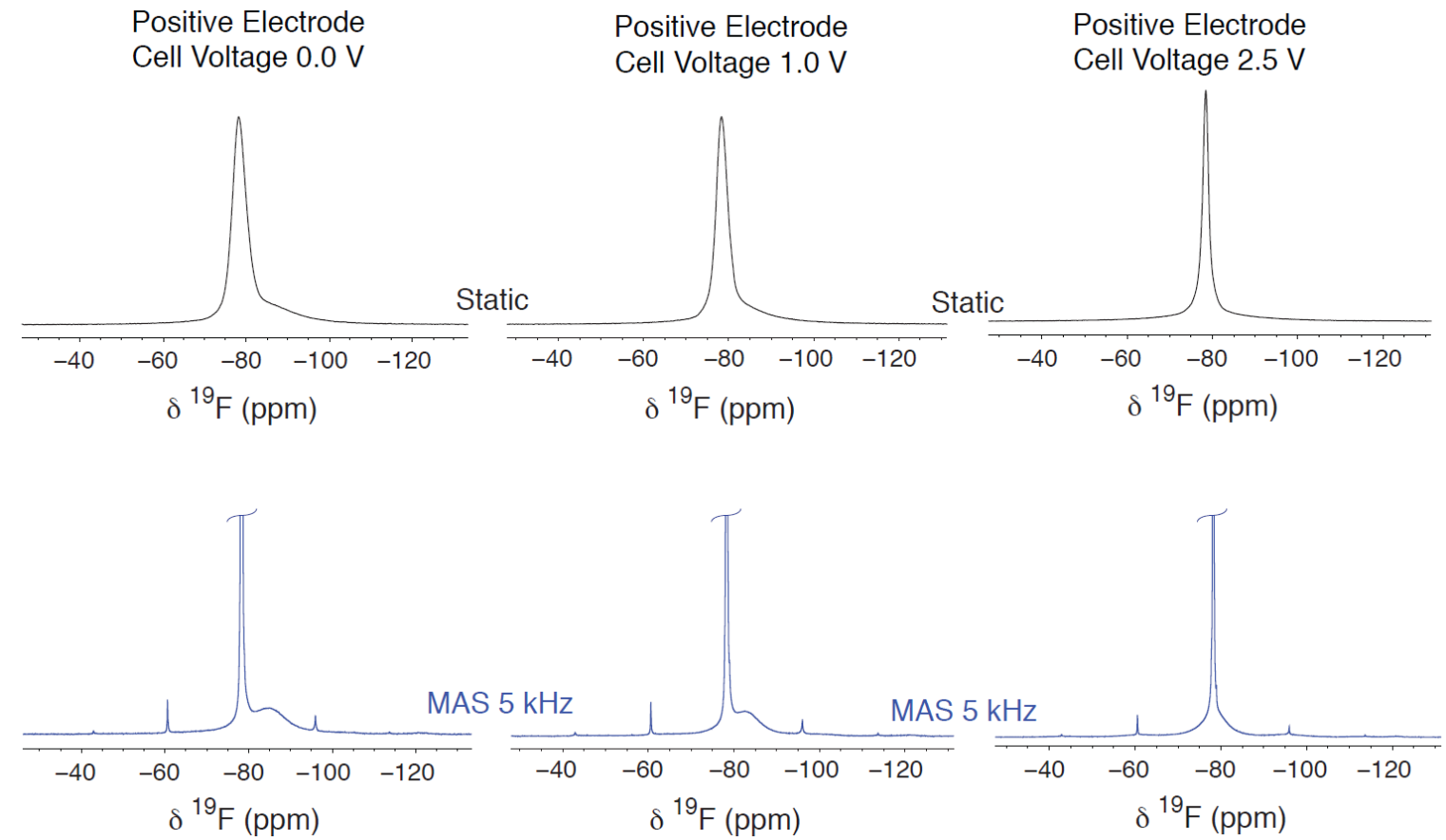




H. WANG *et al.*, *J. Am. Chem. Soc.*, **133**, 19270 (2011)

Ex situ NMR and Magic Angle Spinning (MAS) for ILs

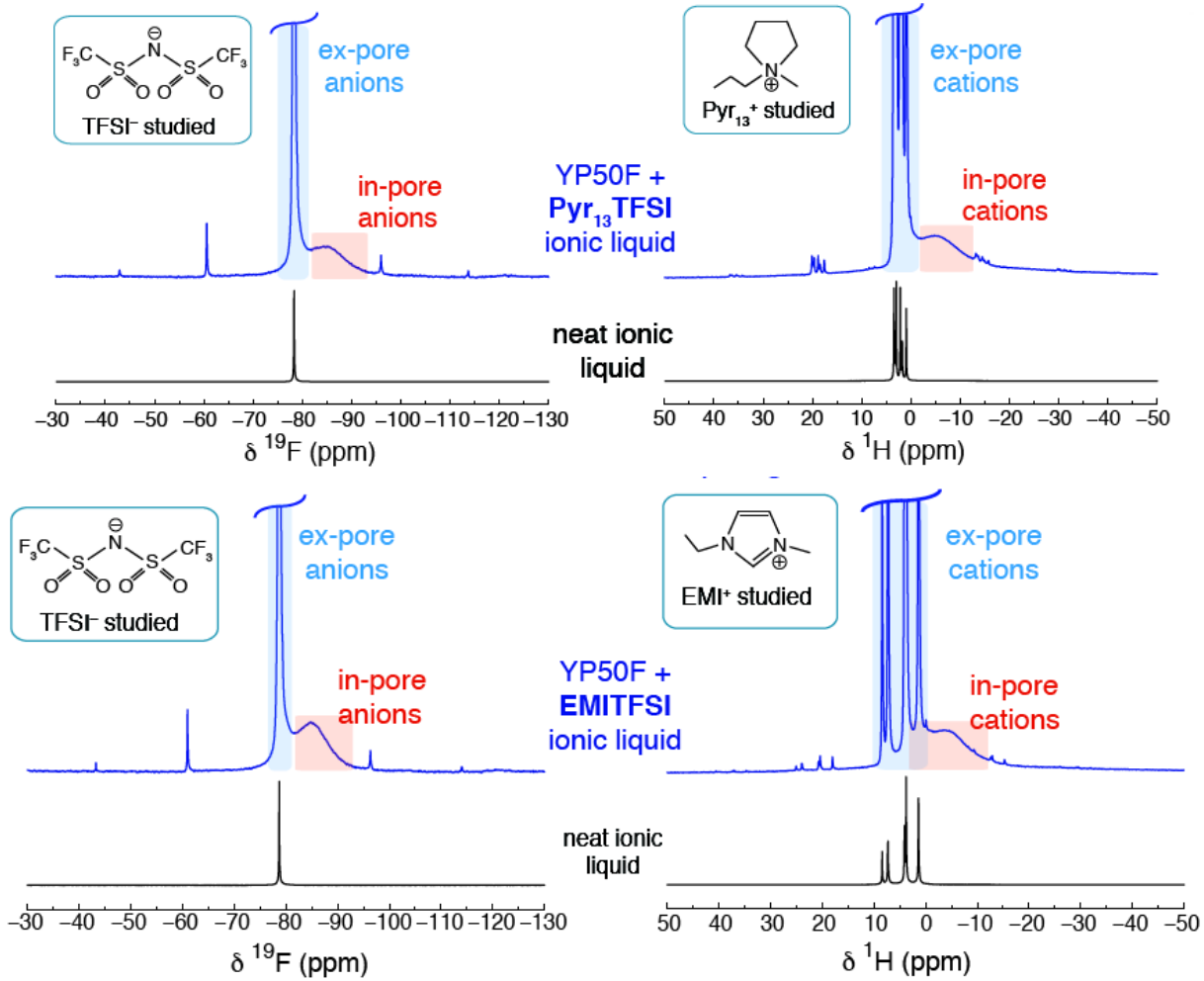
- YP-50F and [Pyr_{13}][TFSI]
- Cell dismantled before acquiring the spectra



A. FORSE *et al.*, *J. Am. Chem. Soc.*, **137**, 7231 (2015)

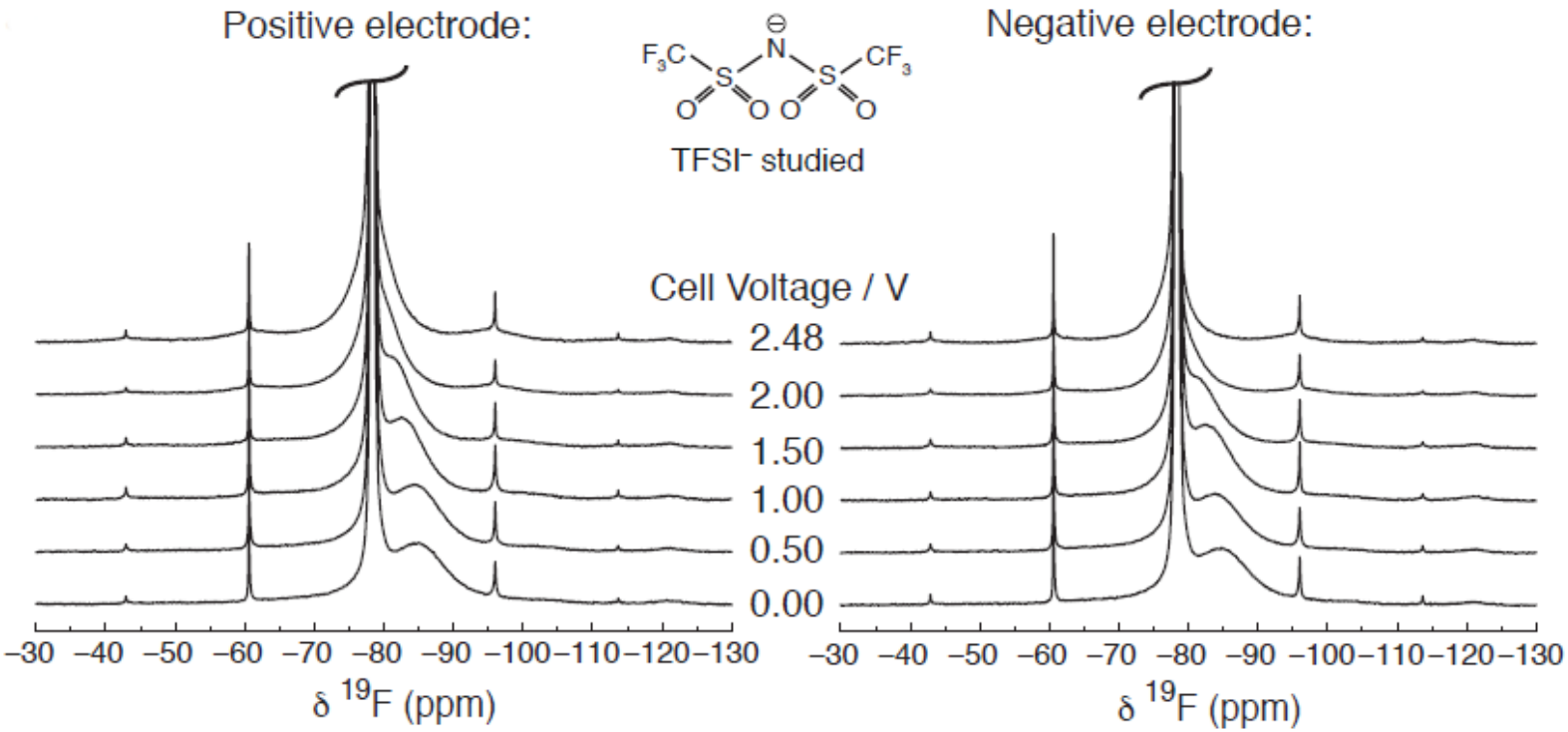
ILs and YP-50F: unpolarised carbon

- Possibility to study anions and cations separately



A. FORSE *et al.*, *J. Am. Chem. Soc.*, **137**, 7231 (2015)

[Pyr13][TFSI] and YP-50F: *Ex situ* spectra

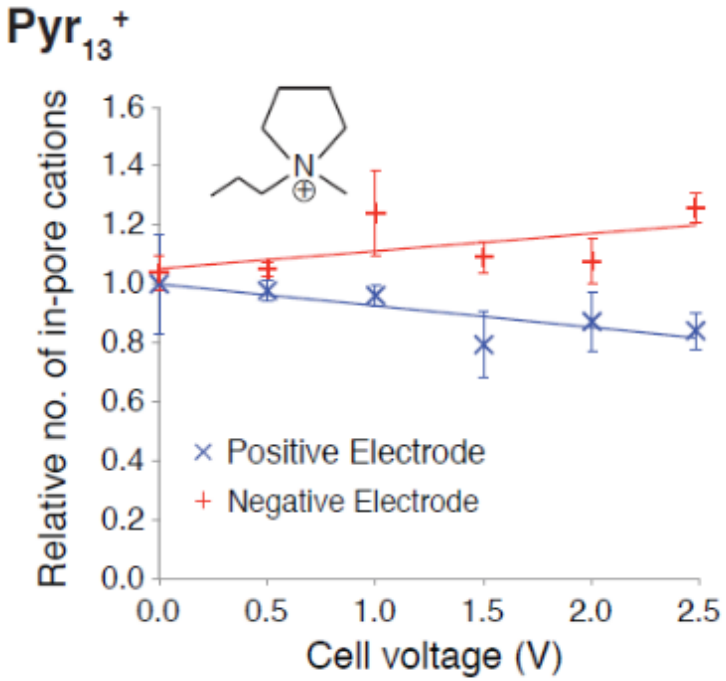


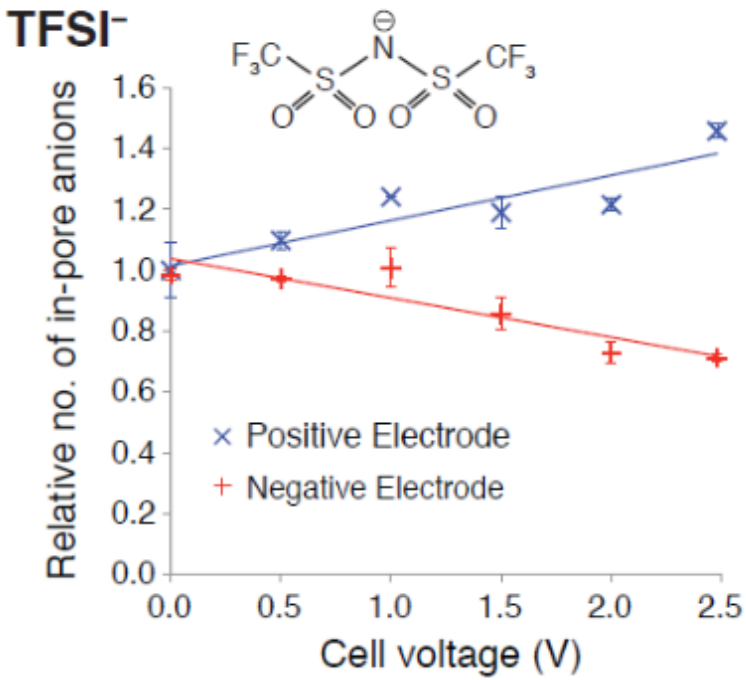
- As for organic electrolytes, the shift becomes more positive with larger applied potentials.

A. FORSE *et al.*, *J. Am. Chem. Soc.*, **137**, 7231 (2015)

[Pyr13][TFSI] and YP-50F: mechanical insights

- Anions more involved in the charging, in both electrodes





- Mechanism different from what was seen in the organic electrolyte

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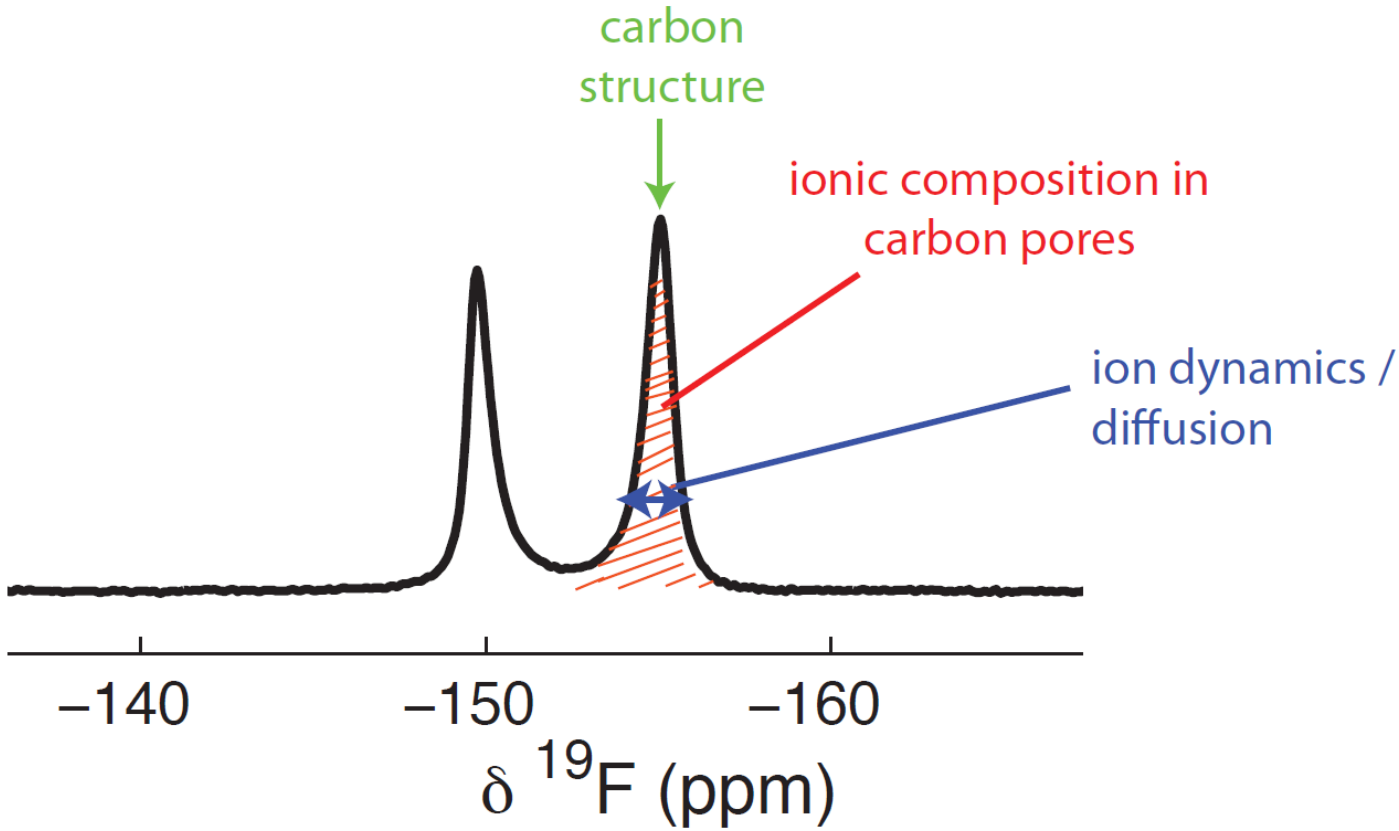
A. FORSE *et al.*, *J. Am. Chem. Soc.*, **137**, 7231 (2015)

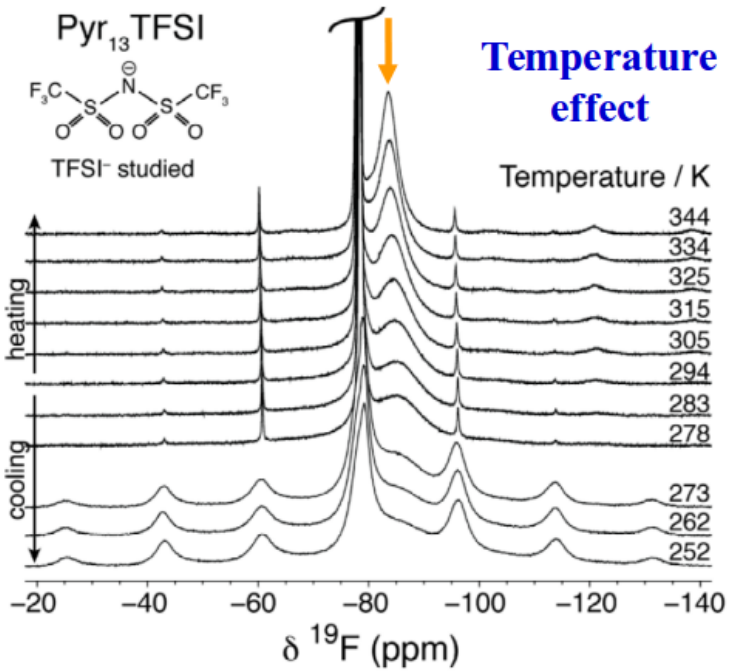
NMR peak: 3 sources of information

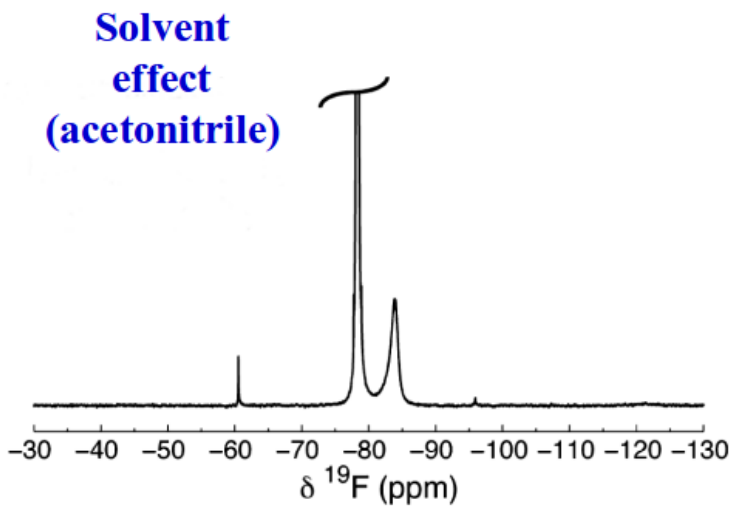


- Quantity of adsorbed ions from area under the peak
- Information on the dynamics from the linewidth
- Combined experimental and theoretical study to learn about the carbon structure

[Pyr13][TFSI] and YP-50F: lineshape and ion dynamics

- Higher temperatures → faster dynamics → sharper peaks





- Addition of solvent → faster dynamics → sharper peak
- Relative comparison of ion dynamics
- What about the absolute vale of the linewidth?

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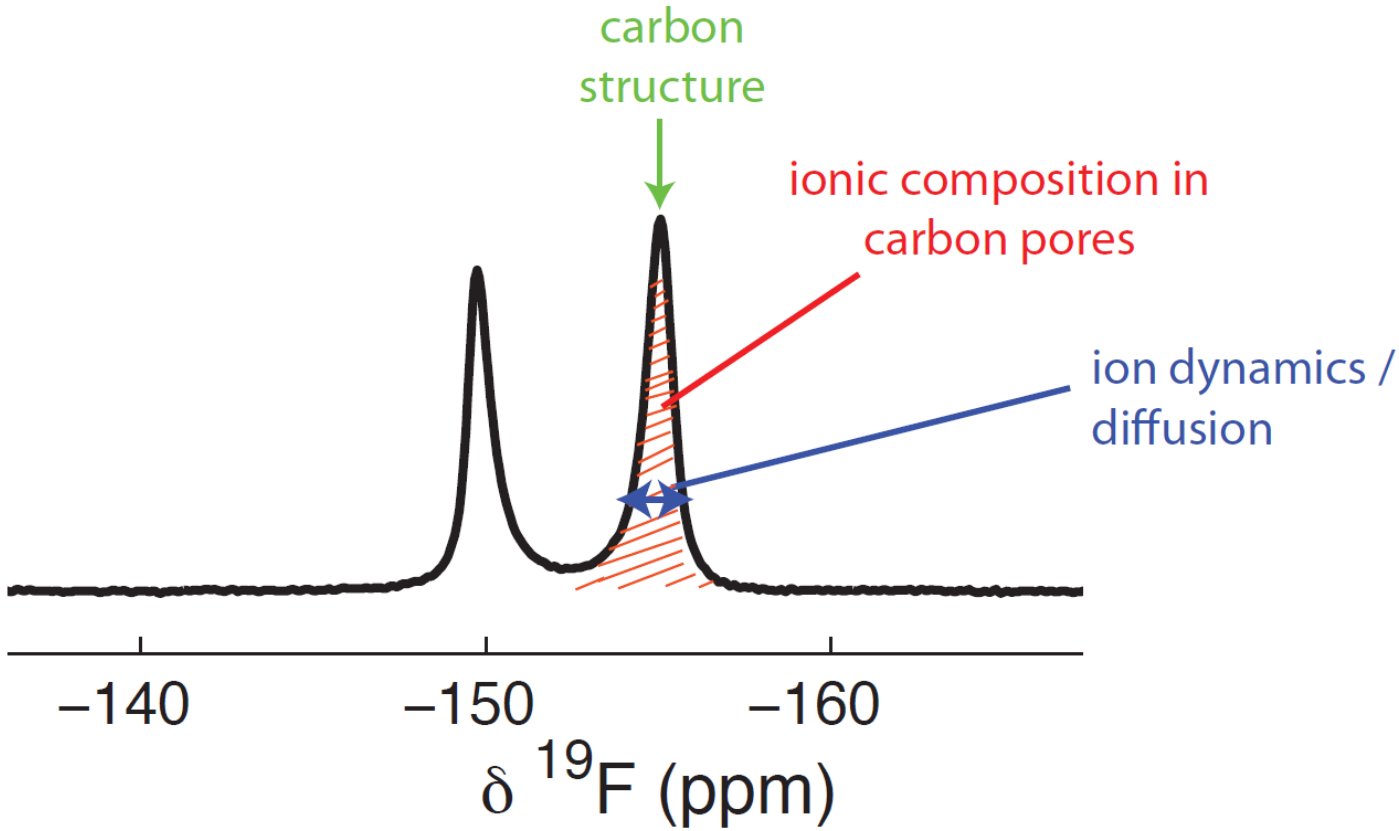
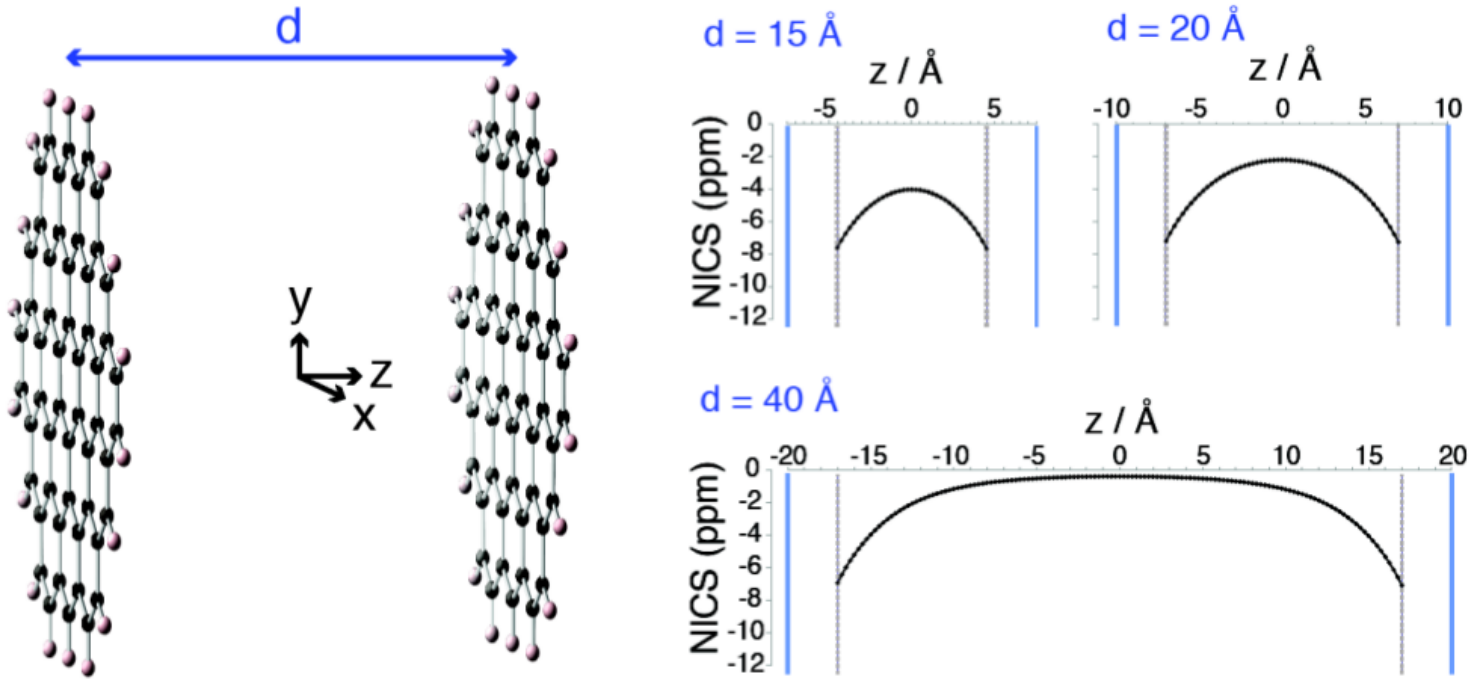
NMR peak: 3 sources of information



- Quantity of adsorbed ions from area under the peak
- Information on the dynamics from the linewidth
- Combined experimental and theoretical study to learn about the carbon structure

Ring currents and nucleus independent chemical shifts

- Experimentally: shift independent of the nucleus studied

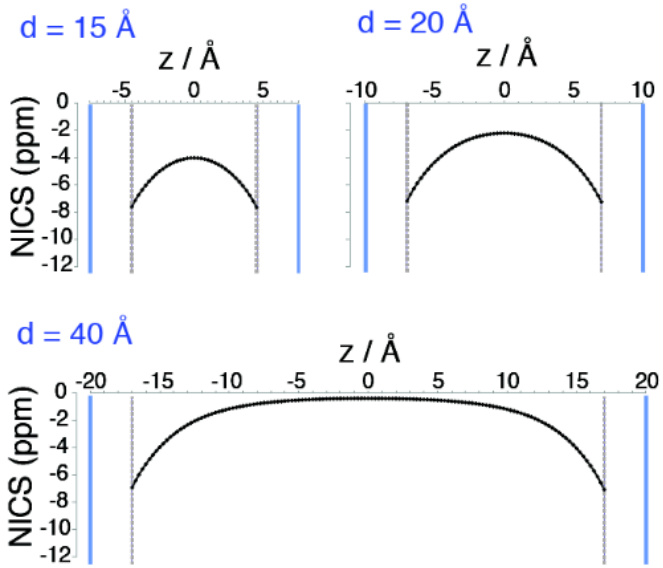


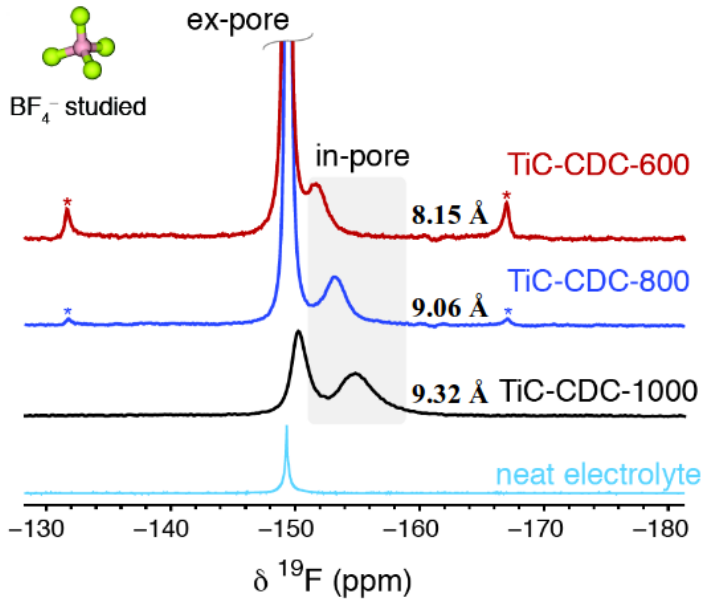
- Estimation of the NICS from DFT calculations
- In agreement with a shift to lower frequencies
- Dynamics? Pore size distribution (PSD)? Order?

A. C. FORSE *et al.*, *J. Phys. Chem. C*, **118**, 7508 (2014)

Disagreement between experiments and calculations?

- From NICS: shift smaller for larger pores



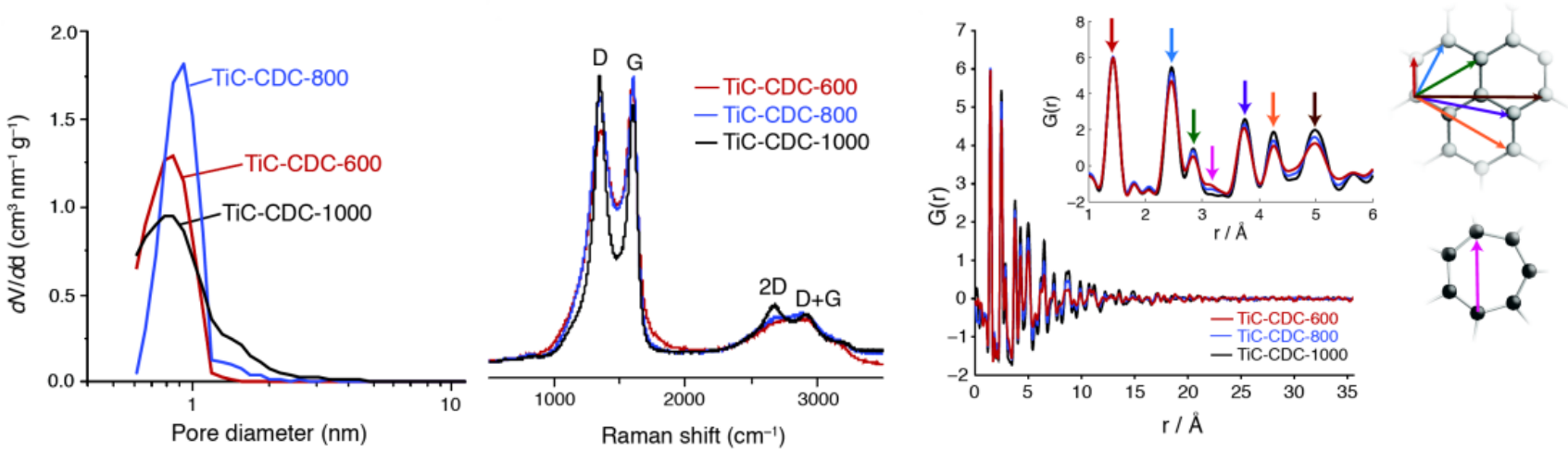


- Experimentally: shift larger for larger pores
- At least two effects:
  → Pore Size Distribution (PSD)
  → Order
- Inclusion of diffusion?

A. C. FORSE *et al.*, *J. Phys. Chem. C*, **118**, 7508 (2014)

Two effects: PSD and order

- PSD from adsorption isotherms (Presser group)
- Raman (Presser group):
  $\rightarrow$ order increases when increasing the synthesis temperature
- PDF (Phoebe):
  $\rightarrow$ seems in agreement with Raman

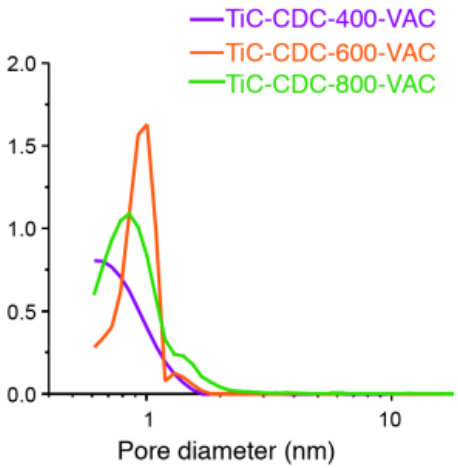


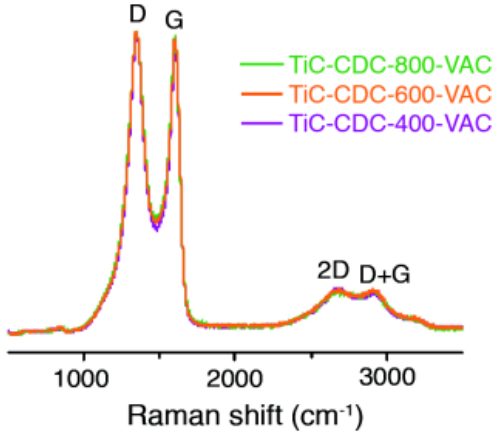
- Order as well as average pore size increase when increasing the synthesis temperature.

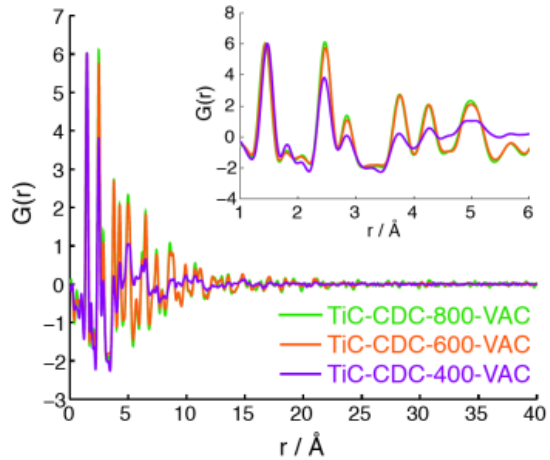
A. C. FORSE *et al.*, *Chem. Mater.*, **in press**

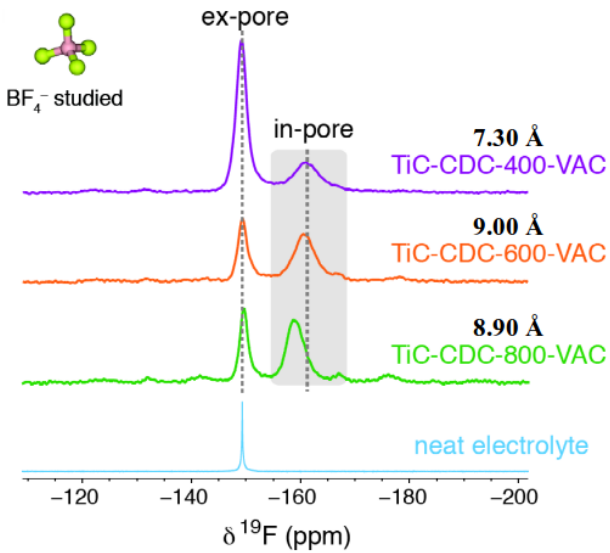
Exploration of the PSD effect through experiments

- Vacuum-annealing at 1400°C to obtain a similar order







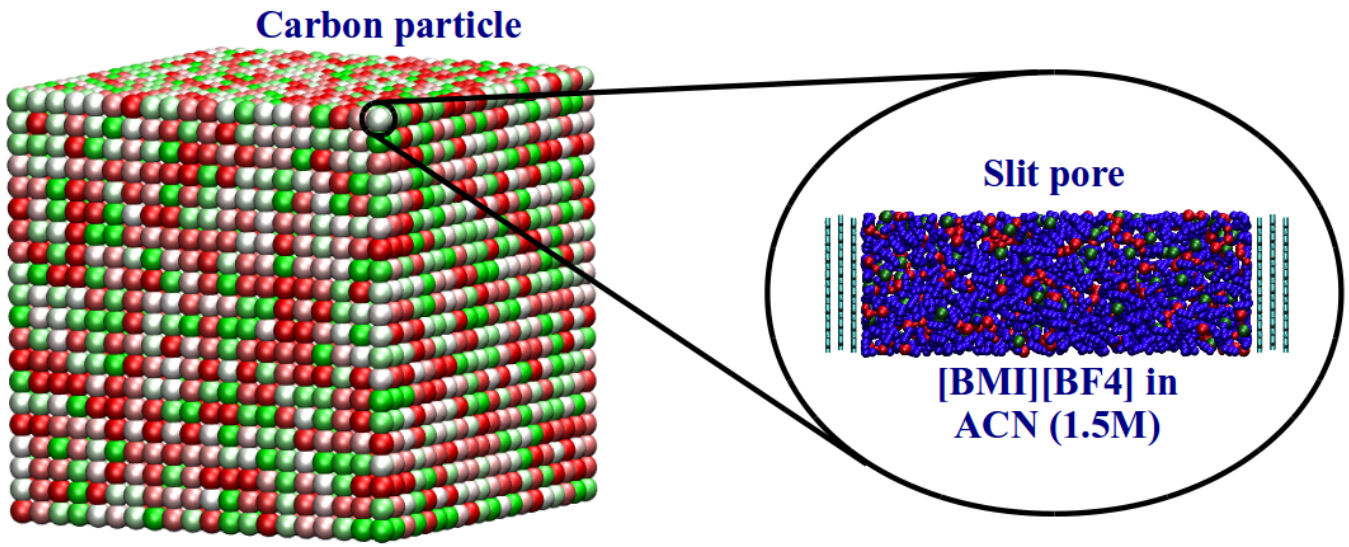


- Small effect of PSD
- Average pore size insufficient to explain the trend observed
- Presence of large pores in CDC-VAC-800

A. C. FORSE *et al.*, *Chem. Mater.*, **in press**

Predicting NMR spectra for carbon particles

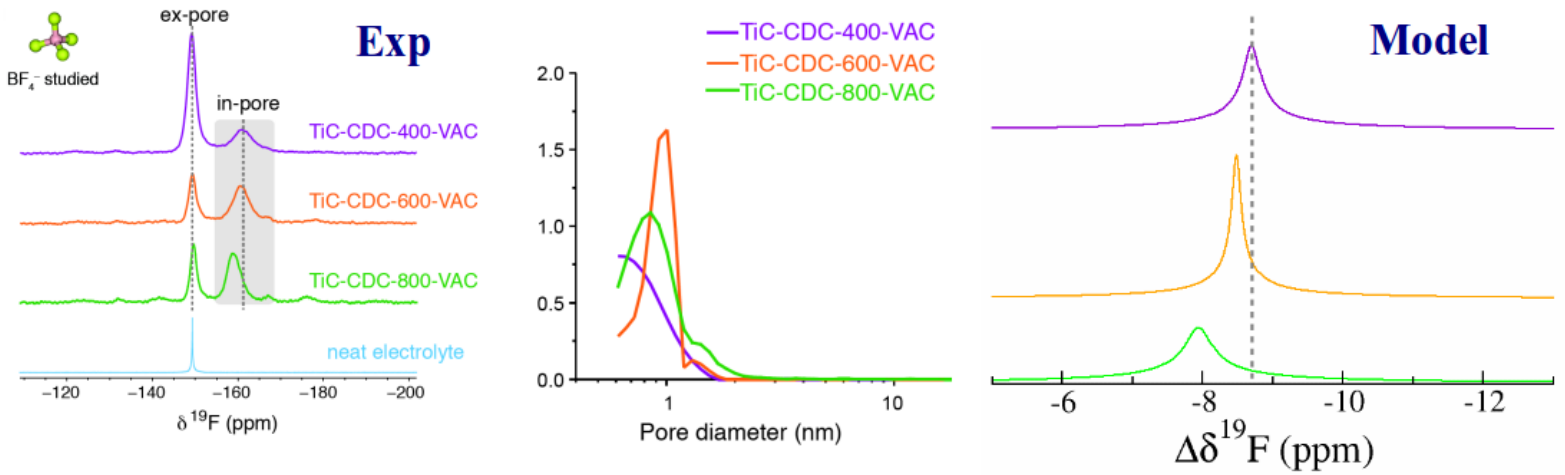
- Lattice model: NMR spectra of ions diffusing in a carbon particle consisiting of slit pores
- Each pore is characterised by:
  → a pore size (PSD from exp.)
  → a quantity of adsorbed ions (MD)
  → a chemical shift (DFT)



- Ions diffuse through the carbon particle
- Only in-pore ions → only one peak in the NMR spectrum

Exploration of the PSD effect through simulations

- Vacuum-annealed carbons: similar order, different PSDs



- The model includes the diffusion of the ions and the experimental pore size distribution.
- Same trend for the shifts in experiments and simulations
- Linewidth not reliable yet in the model
- Comparison between exp. and model $\rightarrow$ assessment of the order

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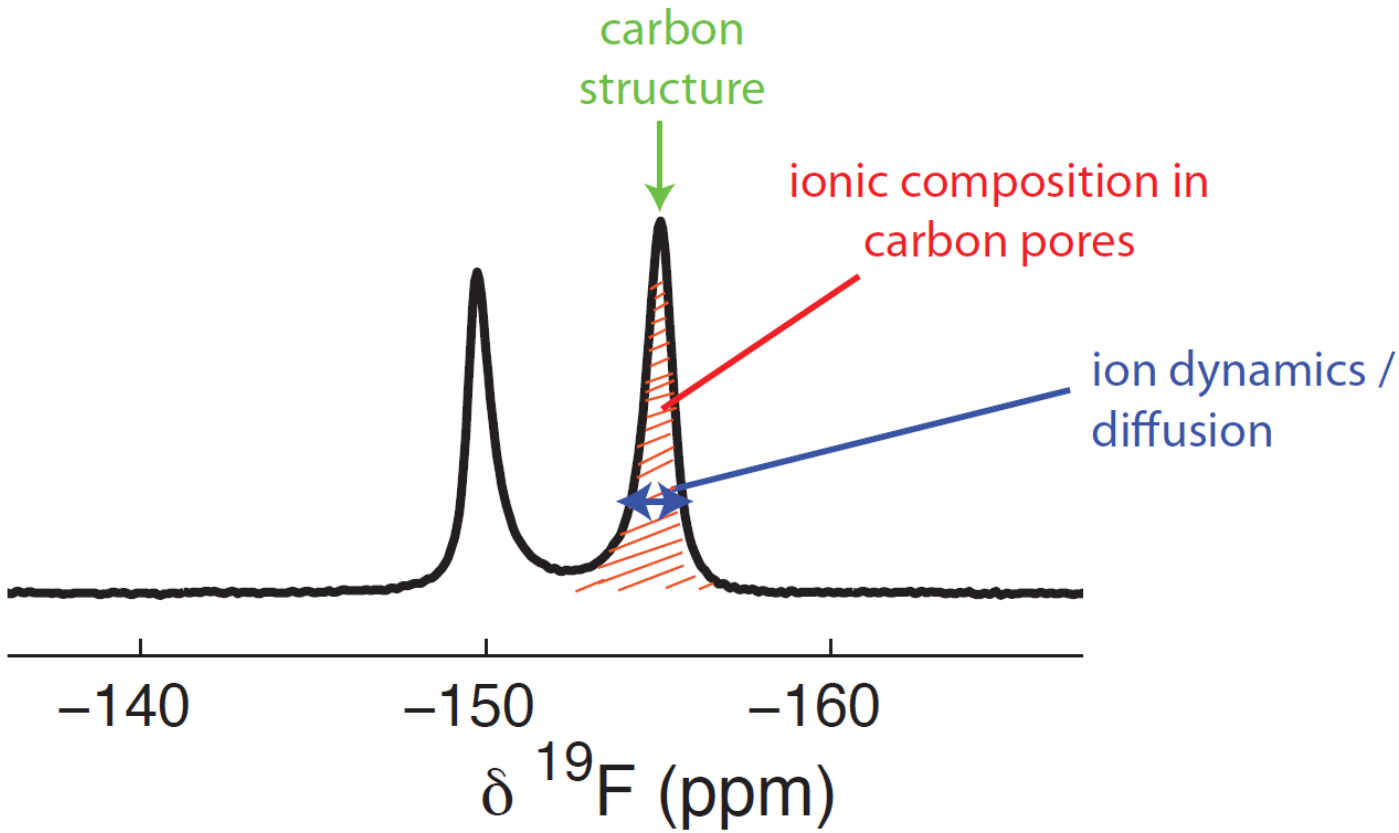
A. C. FORSE *et al.*, *Chem. Mater.*, **in press**

Conclusions



- NMR is a very powerful method to study adsorption of ions in porous materials.
- Combining it with simulations can allow us to go even further.

Acknowledgements

- Clare Grey, Daan Frenkel
- Alex Forse, John Griffin
- Phoebe Allan, Beth Humphreys
- Yury Gogotsi, Volker Presser
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