Experimental report

Proposal:	6-07-3	0		Council: 4/2017			
Title:	Ionic 1	lonic liquids under 1D nanometric confinement in CNT membranes: gigantic transport properties?					
Research area: Materials							
This proposal is a new proposal							
Main proposer:		Jean Marc ZANOTTI					
Experimental team: Jean Marc ZANOTTI							
		Patrick JUDEINSTEIN	N				
Local contacts:		Peter FOUQUET					
		Bernhard FRICK					
Samples: Deuterated polystyrene							
carbon nanotube							
Ionic liquid							
Instrument			Requested days	Allocated days	From	То	
IN16B			6	3	22/05/2018	25/05/2018	
IN11			15	2	12/03/2018	14/03/2018	
Abstract:							

Under confinement inside 1.4 nm Carbon NanoTubes (CNT), water adopts a very specific geometry characterized by a linear configuration of a fraction of the molecules. This peculiar local structure induces unexpected dynamical effects at the macroscopic scale: when forced inside a CNT membrane, water is experimentally found to flow-up three orders of magnitude faster than predicted by the continuum hydrodynamics picture: this is water superlubricity. We have recently extended the results observed on water to the case of neat Ionic Liquids (IL) under CNT confinement. While no dynamical change was detected at the molecular scale (QENS), we have shown a 3 fold enhancement of the IL transport properties at the microscopic scale (PFG). Addition of lithium to the IL has a major influence on the structuration of the IL and should significantly change the local behavior. We propose to probe the CNT confined IL+Li+ local dynamics.

Proposal number: 6-07-30 Title: Ionic liquids under 1D nanometric confinement in CNT membranes: gigantic transport properties?

We proposed to investigate Ionic Liquids (IL) under confinement in carbon nanotube (CNT) membranes. Using 1D CNT nanometric confinement we target to reach ILs superlubricity as observed in the case of water confined in CNT. The 1D CNT membrane could turn to be a remarkable battery separator: they show no tortuous pathway of lithium ions traveling between the electrodes, and no friction at the CNT / ILs interface, enhancing the electrolytes transport properties and thus the power density of batteries.



Figure 1. a) Schematic view of the 1D CNT membrane. Deuterated polystyrene (in yellow) has been used for the experiment (Mw 350000 g/mol, Tg ~110°C). The CNT (in gray) are 4nm in diameter. SEM image of the CNT membrane. The porosity of the CNT membrane is ~ 6%.

In this experiment on IN16B we have measured the temperature dependence of elastic (EFWS) and inelastic (IFWS) intensities from 2K to 350K. IN16B data show that, a diffusive behavior (dispersive in Q in Figure 2) activates at lower temperatures under confinement in CNT membrane than in bulk: a shift of approximately 25°C is observed. This result suggests that at 300K the nanometric mobility is faster under confinement than in bulk, which is consistent with the conductivity gains we observed (factor up to 50 upon CNT confinement).^{1,2}



Figure 2. IFWS measured on IN16B (at 2 μ eV) for both bulk (right) and confined (left) IL based electrolyte (BmimTFSI + 1M LiTFSI, ~ 5mg @ CNT). Data are shown at 3 Q-values (0.6, 1 and 1.4 A⁻¹) revealing a Q-dispersive mode, that can be attributed to nanometric diffusion. Solid lines are guide to the eye. A shift of about 25°C is observed under CNT confinement revealing a strong confinement effect.



Figure 3. IFWS measured on IN16B for both bulk (right, 2µeV 5µeV and 10µeV) and confined (left, 2µeV) IL based electrolyte (BmimTFSI + 1M LiTFSI, ~ 5mg @ CNT). Data are averaged over the whole Q-range. IFWS of the empty CNT membrane has also been performed (left, dark blue): the inelastic intensity observed in light blue can clearly be attributed to the confined IL. A shift of about 25°C is observed under CNT confinement revealing a strong confinement effect.

Unfortunately, the amount of IL confined in the membrane was too low for IN11.

We now need to perform QENS measurements on IN16B at selected temperatures to determine the diffusion coefficient of IL within the CNT to evaluate the effect of the confinement on the nanosecond time scale. These information are crucial to understand the ion conduction mechanism in this material.

REFERENCES.

¹ Q. Berrod, P. Judeinstein, Y. Fu, V.S. Battaglia, A. Fournier, J. Dijon, and J.-M. Zanotti, ArXiv:1710.06020 [Cond-Mat] (2017).

² Q. Berrod, F. Ferdeghini, P. Judeinstein, N. Genevaz, R. Ramos, A. Fournier, J. Dijon, J. Ollivier, S. Rols, D. Yu, R.A. Mole, and J.-M. Zanotti, Nanoscale **8**, 7845 (2016).