# The fate of water at the electrochemical interfaces: electrochemical behavior of free water vs. coordinating water.

Nicolas Dubouis,<sup>a,b,¶</sup> Alessandra Serva,<sup>c,¶</sup> Elodie Salager,<sup>b,d</sup> Michael Deschamps,<sup>b,d</sup> Mathieu Salanne,<sup>b,c</sup>\* Alexis Grimaud<sup>a,b</sup>\*

### **AUTHORS ADDRESS:**

<sup>a</sup> Chimie du Solide et de l'Energie, Collège de France, UMR 8260, 75231 Paris Cedex 05, France

<sup>b</sup> Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR3459, 33 rue Saint Leu, 80039

Amiens Cedex, France

° Sorbonne Université, CNRS, Physico-Chimie des Électrolytes et Nanosystèmes Interfaciaux, F-75005

Paris, France

<sup>d</sup> CNRS, CEMHTI UPR3079, Université d'Orléans, 1D avenue de la recherche scientifique, 45071

Orléans Cedex 2, France

<sup>¶</sup> These authors contributed equally to the work

emails: mathieu.salanne@sorbonne-universite.fr, alexis.grimaud@college-de-france.fr

## Table of contents

Experimental and simulation details	3
Materials and methods	3
Electrochemical measurements	3
Nuclear Magnetic Resonance (NMR) Spectroscopy	3
Molecular Dynamics simulation details	3
Figure S1: Cyclic Voltammetry in dry electrolytes	5
Figure S2: Cation-Acetonitrile radial distribution functions	5
Figure S3: Cage correlation function used to determine the residence lifetime of H <sub>2</sub> O in cations first solvation shell	6
Figure S4: Divalent cation vs. monovalent cations	6
Figure S5: Cyclic Voltammetry in EC:DMC electrolytes containing 10,000 ppm of water	7
Supporting information references	7

#### **Experimental and simulation details**

#### Materials and methods

All the experiments (electrolytes preparation and electrochemical tests) were conducted in an argon filled glovebox (H<sub>2</sub>O and O<sub>2</sub> contents < 0.5 ppm). Prior to use, all the glassware was rinsed at least 3 times with Milli-Q water before being dried at 80°C for at least one hour. Lithium perchlorate (Alfa Aesar, anhydrous, 99%), sodium perchlorate (Alfa Aesar, Battery Grade) and tetrabutylammonium perchlorate (Sigma-Aldrich, > 99.0%) were dried at 80°C in a Büchi vacuum oven for at least 12 hours before being transferred without exposure to the air to the glovebox. Extra Dry acetonitrile (Acros organics; 99.9%, AcroSeal®, over molecular sieves) was used for the preparation of the electrolytes. Its water content was checked to be < 10 ppm by Karl-Fischer titration. Dry electrolytes were prepared by precisely weighting a mass of salt and adding the corresponding volume of solvent to obtain the desired molarity. Wet electrolytes were prepared in the same way, except that the acetonitrile used was prepared by deliberately adding a precise mass of water with the aid of a micro syringe into a vial sealed with a silicon septum cap (water content was checked by Karl-Fischer titration).

#### **Electrochemical measurements**

Data were acquired either on a Biologic VSP or Biologic VMP3 potentiostat. Prior to any measurement, mirror polished glassy carbon (GC) electrodes and platinum electrodes (Pine research) were polished using ultrafine alumina slurries (0.05  $\mu$ m on microcloth polishing disk for the GC, and three steps for the Pt starting from 5  $\mu$ m on nylon polishing disk, followed by 0.3  $\mu$ m and 0.05  $\mu$ m on microcloth polishing disk). Residual traces of slurries were removed by sonicating the as polished electrodes in a 50:50 H<sub>2</sub>O:EtOH solution two times for 15 minutes. To ensure the cleanliness of platinum electrodes surface, platinum electrodes were hold at + 2.0 V vs. SHE in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for 2 minutes followed by 10 cycles of cyclic voltammetry (from 1.350 V to 0.0 V vs. SHE) in the same H<sub>2</sub>SO<sub>4</sub> solution. Then, freshly cleaned electrodes were rinsed with ultrapure water, air-dried and pumped in the glovebox antechamber. All electrochemical measurements were recorded using a three electrodes cell setup with an Ag/Ag<sup>+</sup> organic reference electrode (regularly calibrated against ferrocene). A platinum wire was used as a counter electrode for all measurements (flame annealed between all the measurements). For static measurements, electrodes were immersed in a small volume of electrolyte (typically 5 mL). A sweep rate of 50 mV.s<sup>-1</sup> was used in all the cyclic voltammetry experiments.

Ohmic drop was measured using current-interrupt technique after every electrochemical measurement. Typical values of around 90  $\Omega$  were obtained. The ohmic drop compensation was performed during the data treatment (85% of correction, as suggested by the potentiostat manufacturer).

#### Nuclear Magnetic Resonance (NMR) Spectroscopy

Liquid-state NMR spectra were recorded on a Bruker 7.046 T Avance III HD NMR spectrometer mounted with a 5 mm HX(F) probehead. For electrolyte analysis, NMR tubes equipped with a  $D_2O$  (99% D, Sigma-Aldrich) filled coaxial insert were used in order to lock the magnetic field and HOD signal was used as an internal reference (4.7 ppm). Water content of different electrolytes was checked to be in the good range (basically, error of +/-5%). Single pulses sequences were used to record <sup>1</sup>H and <sup>7</sup>Li spectra. 90° pulses were optimized for the 100 mM LiClO<sub>4</sub> in 10,000 ppm H<sub>2</sub>O acetonitrile solution. Experimental parameters used for each nucleus are shown in Table S1.

	·H	Nucleus
4	32	Number of scans
4	0	Dummy scans
10	2	Acquisition time (s)
10	1	Recycle time (s)
4 4 10 10	32 0 2 1	Number of scans Dummy scans Acquisition time (s) Recycle time (s)

Table S1. Experimental parameters used in the NMR experiments.

#### **Molecular Dynamics simulation details**

Classical MD simulations of 0.1 M perchlorate salts (LiClO<sub>4</sub>, NaClO<sub>4</sub> and TBAClO<sub>4</sub>, with TBA<sup>+</sup> = tetrabutylammonium cation) + 10,000 ppm of water in acetonitrile have been performed using the GROMACS software package.<sup>1</sup> The acetonitrile solvent was

described with the six-site model developed by Grabuleda et al.,<sup>2</sup> which provides a good description of bulk liquid acetonitrile, while the SPC/E model was adopted for water molecules.<sup>3</sup> As regards the perchlorate salts, the force field parameters for TBA<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> ions were taken from Ref. 4 and Ref. 5, respectively, while the Lennard-Jones parameters for Li<sup>+</sup> and Na<sup>+</sup> were taken from Åqvist.<sup>6</sup> Mixed Lennard-Jones parameters for all of the different atom types were obtained from the Lorentz-Berthelot combination rules.

The simulations were performed in the NVT ensemble at 300 K, with the Nosé-Hoover thermostat<sup>7,8</sup> (the relaxation constant used is 0.5 ps), using a timestep of 1 fs and saving a configuration every 100 fs. For each simulation the system was composed of 5 cations, 5 anions, 22 water molecules and 965 acetonitrile molecules, placed in a cubic box and replicated using periodic boundary conditions. The initial configuration was achieved by generating a low density cubic box by means of the PACKMOL package,<sup>9</sup> that was then compressed in the NPT ensemble in order to reproduce the acetonitrile density (0.786 g/cm<sup>3</sup>) at temperature and pressure conditions of 300 K and 1 atm, respectively. The box length obtained were 44.08 Å, 44.08 Å and 44.95 Å for LiClO<sub>4</sub>, NaClO<sub>4</sub> and TBAClO<sub>4</sub>, respectively. The systems were then equilibrated in the NVT ensemble at 700 K for 0.5 ns, followed by a final NVT equilibration at 300 K for 2 ns. The production simulations were finally carried out in the NVT ensemble at 300 K for 100 ns. Long-range electrostatic interactions were computed with the particle mesh Ewald method,<sup>10</sup> while a cutoff distance of 9 Å was adopted for the nonbonded interactions. The LINCS<sup>11</sup> algorithm was employed to constrain the stretching interactions involving hydrogen atoms.

The structural properties of the systems have been characterized by calculating Cation-Water radial distribution functions and Cation-Water coordination numbers. The latter have been obtained by the integration of the first peak up to a cutoff distance defined as the position of the first minimum of the corresponding RDF. The cutoff used here are 2.57 Å, 3.30 Å and 5.60 Å for Li- $O_{water}$ , Na- $O_{water}$  and TBA- $O_{water}$ , respectively. Note that the nitrogen atom has been used for the TBA<sup>+</sup> cation. The Cation-Water residence times were extracted using a cage correlation function analysis.<sup>12</sup>

Radial distribution function and coordination number analysis have been performed using the GROMACS package,<sup>1</sup> while the cation-water cage lifetimes have been calculated by means of in-house developed codes. The VMD software<sup>13</sup> has been used to obtain snapshots from the MD simulations.



**Figure S1.** Cyclic voltammograms recorded at 50 mV.s<sup>-1</sup> on a platinum electrode in dry acetonitrile electrolytes containing 100 mM of LiClO<sub>4</sub> (purple) or TBAClO<sub>4</sub> (orange). The cathodic current at ~ 0.3 V vs. SHE can be attributed to platinum surface electrochemistry (for instance, Pt-OH desorption).

Figure S2: Cation-Acetonitrile radial distribution functions



Figure S2. Cation-N<sub>ACN</sub> radial distribution functions (RDFs calculated from the MD simulations of Li/NaClO<sub>4</sub> in H<sub>2</sub>O/ACN).



**Figure S3.** Cage correlation function used to determine the residence lifetime of  $H_2O$  in cations first solvation shell for the LiClO<sub>4</sub> (purple), NaClO<sub>4</sub> (green), TBAClO<sub>4</sub> (orange) simulations. The characteristic time of the exponential decay was measured at 37% of the cage function value for t=0 ps.





**Figure S4.** Extension of the study to more hydrophobic divalent cation  $Mg^{2+}$  showing (left) the NMR spectrum of 100 mM of  $Mg(ClO_4)_2(H_2O)_6$  (pink) in dry ACN compared to the spectra of monovalent cations (Li<sup>+</sup>: purple, Na<sup>+</sup>: green, TBA<sup>+</sup>: orange) perchlorate salts (100 mM in 10,000 ppm H<sub>2</sub>O containing ACN) and (right) corresponding cyclic voltammetry over a platinum electrode (sweep rate: 50 mV/s. On the NMR spectra, peaks corresponding to acetonitrile are labeled \* while those corresponding to HOD in D<sub>2</sub>O capillary are labeled °.



**Figure S5.** Cyclic voltammograms recorded at 50 mV.s<sup>-1</sup> on a platinum electrode in ethylene carbonate:dimethyl carbonate (1:1 in mass) electrolytes containing 10,000 ppm of water and 100 mM of  $LiClO_4$  (purple) or TBAClO<sub>4</sub> (orange).

#### Supporting information references

- 1 H. J. C. Berendsen, D. van der Spoel and R. van Drunen, Comput. Phys. Commun., 1995, 91, 43-56.
- 2 X. Grabuleda, C. Jaime and P. A. Kollman, J. Comput. Chem., 2000, 21, 901–908.
- 3 H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, J. Phys. Chem., 1987, 91, 6269-6271.
- 4 D. Bhowmik, N. Malikova, G. Mériguet, O. Bernard, J. Teixeira and P. Turq, *Phys. Chem. Chem. Phys.*, 2014, 16, 13447-13457.
- 5 X. Liu, S. Zhang, G. Zhou, G. Wu, X. Yuan and X. Yao, J. Phys. Chem. B, 2006, 110, 12062–12071.
- 6 J. Aqvist, J. Phys. Chem., 1990, 94, 8021-8024.
- 7 S. Nosé, J. Chem. Phys., 1984, 81, 511-519.
- 8 D. J. Evans and B. L. Holian, J. Chem. Phys., 1985, 83, 4069-4074.
- 9 L. Martínez, R. Andrade, E. G. Birgin and J. M. Martínez, J. Comput. Chem., 2009, 30, 2157-2164.
- 10 U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee and L. G. Pedersen, J. Chem. Phys., 1995, 103, 8577-8593.
- 11 B. Hess, H. Bekker, H. J. C. Berendsen and J. G. E. M. Fraaije, J. Comput. Chem., 1997, 18, 1463-1472.
- 12 E. Rabani, J. D. Gezelter and B. J. Berne, J. Chem. Phys., 1997, 107, 6867-6876.
- 13 W. Humphrey, A. Dalke and K. Schulten, J. Mol. Graph., 1996, 14, 33-38.