

**Supplementary Information for: Uranyl (UO_2^{2+})
Structuring and Dynamics at
Graphene/Electrolyte Interface**

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Force Fields Benchmarking

To probe the sensitivity of the uranyl adsorption (at the graphene surface) towards the ion charges, the ion (UO_2^{2+} , Li^+ and NO_3^-) charges were scaled from 75% to 100% with an increment of 5%. The normalized density shows that uranyl adsorption is sensitive to the ion charges, however, a uranyl excess is observed at each q_i (at least 15 times relative to the bulk). Within this study, we used 90 % ECC, as it reproduces experimentally observed uranyl nitrate association constants in LiNO_3 media.¹ The graphene layer was modeled using amber99² and charmm36³ force fields. The water distribution near the graphene layer is used to compare the force fields. Both force fields showed a similar interaction of water with graphene (Figure S 1A). A similar distribution of water near the graphene surface is observed using ab-initio molecular dynamics simulations.⁴ Therefore, Amber99 force fields were employed for the modeling of graphene in each system.

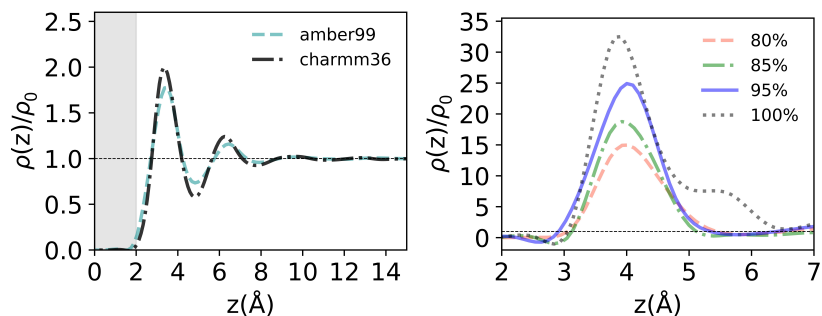


Figure S1: (Left Panel) Normalized density profiles of water along z axis for systems with graphene modeled using amber99 and charmm36 force fields. (Right Panel) The normalized density of uranyl in the interfacial region **I** ($z = 0-8 \text{ \AA}$) at various ECC values in the system with 1.06 M $\text{UO}_2(\text{NO}_3)_2$ and 1.41 M LiNO_3 .

Umbrella Sampling The umbrella sampling methodology was employed to examine the thermodynamics of the ion-graphene interactions. Systems were prepared by inserting one $\text{UO}_2^{2+}/\text{Li}^+$ ions into a orthogonal water/graphene box. Charges were neutralized by placing two & one NO_3^- ions in the system with UO_2^{2+} and Li^+ respectively. Free energy calculations were performed with the GROMACS⁵ software package patched with Plumed.⁶ The z distance (d_z) between ion and graphene center of mass (COM) was selected as a collective variable (CV) for generating the potential of mean forces (PMFs) with 0.2 nm sampling windows and 500 kcal/(mol nm²) harmonic restraint. An additional constraint was applied to keep the ion in a cylindrical space along the z axis (d_z) to make the calculation faster. PMFs were generated using the weighted histogram analysis method (WHAM). Each sampling window was equilibrated in the NPT ensemble for 0.5 ns and the final production data were collected for 2.0 ns.

Table S1: Average residence times of uranyl as a function of the distance from the graphene surface. Residence times were computed using bin widths of 2 Å.

| Slab number | Slab range Å | τ (ps) |
|-------------|--------------|-------------|
| 1 | 3-5 | 587.196 |
| 2 | 5-7 | 22.808 |
| 3 | 7-9 | 19.585 |
| 4 | 9-11 | 20.945 |
| 5 | 11-13 | 8.563 |
| 6 | 13-15 | 8.863 |

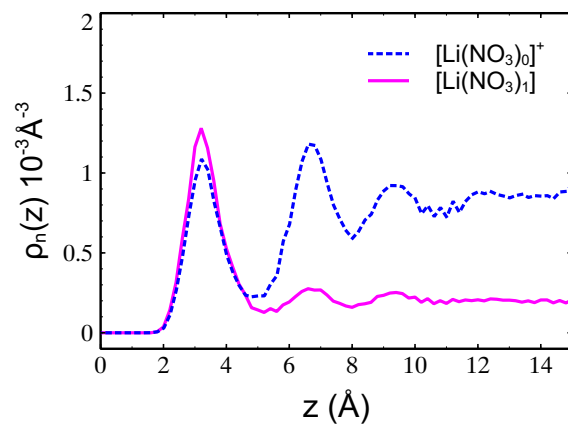


Figure S2: Number density of $[\text{Li}(\text{NO}_3)_n]^{1-n}$ ($n = 0-1$) complexes along the z axis.

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