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Quantitative determination of rare-earth cations distribution at the electrolyte silica interface using x-ray standing waves and molecular dynamics

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A precise understanding of the distribution of chemical species at interfaces, in particular ions, is crucial in many areas.
For example, the so-called Solid-Electrolyte Interface (SEI) plays a crucial role on battery performance.
In a different area, the interaction between ions, humics and minerals plays a key role in the dispersion of pollutants as the modulation of the effective surface charge by ion-surface interactions is affecting the structure of the electric double layer, hence the interaction between charged particles in aqueous solutions and floculation and precipitation.
Rare earth elements of high purity are critical for many industries and their recycling is essential to build a circular economy.
A widely used method for the separation of lanthanides is ion exchange - cation exchange with elution by complexing agents - In these processes, the order of elution of the different rare earth elements depends on the values of the stability constants of the complexes formed with a solid.

From a fundamental point of view, ions at the aqueous -solid interface also exhibit a range of fascinating phenomena, depending on the surface charge, ion valency, concentration, with sometimes extremely surprising and counter-intuitive behavior.
Looking at ionic distributions at the solid-aqueous interface offer a unique way to look at subtle effects related to polarization, hydration,… which would be very difficult to observe otherwise, with often very different behavior with ions with similarly charge and valency.

Based on previous work [1], we have developed a fully quantitative method that gives access to the detailed composition of the first Angstroms at the silica - electrolyte interface. Standing waves generated in a submicron electrolyte layer by Bragg reflection on W-Si multilayers with a 2nm period are used to excite fluorescence from the ions under consideration. Using a thin Cr reference layer in the multilayer, fully quantitative analysis of fluorescence intensity combined with reflectivity measurements allows us to precisely determine the electrolyte film thickness.
Several mixtures of rare earth chlorides and perchlorates were investigated, competitive adsorption being used to enhance differences between rare earth cations and increasing accuracy.

Adsorption is so strong that our results cannot be satisfactorily described by a classical Gouy-Chapman-Stern Model.
Instead, we observe a fairly good agreement with distribution profiles over the entire electrolyte layer based on original molecular dynamics simulations fully taking into account short and long range interactions [2].
Surprisingly, we observe up to 3 adsorption layers, explaining the strong adsorption and the failure of classical models.

[1] F. Malloggi et al., J. Phys. Chem. C 2019, 123, 30294–30304.
[2] B. Siboulet et al., J. Phys. Chem. C 2017, 121, 6756–6769.

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Thin films and interfaces in soft matter and materials science

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