Supplementary Information:

Influence of a Silver salt on the Nanostructure of a Au(111)/Ionic Liquid Interface: an Atomic Force Microscopy Study and Theoretical Concepts

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A   Parameters

The parameters for the ionic liquid $[Py_{1,4}]$TFSA are enlisted in Table 1. The parameters for mass density and conductivity of the ionic liquid have been measured by Iolitec.[1] The value for the relative dielectric constant is taken from the literature.[2] The volume-parameters of the theory, common ionic radius and

Parameter	Value	Source
Density ρ / kg/m^3	$1.40 \cdot 10^3$	[1]
Electric conductivity κ / S/m	$2.10 \cdot 10^{-1}$	[1]
Dielectric constant ε_R	$1.47 \cdot 10^1$	[2]
Particle radius r / nm	$6.70 \cdot 10^{-1}$	calculated
Partial molar volumes v / m^3/mol	$3.02 \cdot 10^{-4}$	calculated

Table 1 System parameters.

common partial molar volume, are both experimentally hardly accessible. We take a naive approach and define the common partial molar volume as the volume given by $v = M/\rho$. The total molar mass of the ionic liquid is given by the sum of the ionic masses, where the silver ions do not contribute in the massless limit . The complex geometry of the constituents leads to non-trivial packing effects. Such volume-defects cannot be resolved within this framework where we model the ions by hard spheres. As an averaged volume effect, we derive the ionic volume from the molar volume by the ratio $v\eta/N_A$.[3] Here, the constant packing fraction $\eta = 0.64$ corresponds to random packing of hard spheres.[4] Finally, we define the particle radius in terms of the sphere of volume half the ionic volume,

$$\frac{4}{3}\pi r^3 = \frac{\eta v}{2N_A}.$$

(1)

The relevant length scale for the interaction potential is then defined by the closest approach of the ions, $\sigma = 2r$.

We model the interaction potential $\mathscr{F}_{\alpha\beta}$ by the product of a dimensionless shape function f_σ

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weighted by a "Coulombic" dimensional prefactor

$$\mathscr{F}_{\alpha\beta} = \frac{F^2}{4\pi\varepsilon_R\varepsilon\sigma}f_\sigma. \tag{2}$$

As shape function, we choose a Lennard-Jones type, $f_\sigma = a\cos(\pi/2\sigma)/(1+bx)^4$, with scaling-coefficients a, b. Beneath repulsion at short distances, this potential also takes account for attractive van-der-Waals interactions at short distances exceeding the particle extension (see Figure 1). Again, the silver ions do not contribute to the interaction term in the indefinitely diluted, massless and dimensionless limit.

B Computational Details

The simulation set up consists of a one-dimensional system composed of the ionic liquid as electrolyte and an ideal planar electrode. The system length L is sufficiently large to contain the electrochemical surface layer. We erect an equidistant spatial grid and implement the system in Matlab. We solve simultaneously for charge density, convection velocity and the electric potential. The system of differential and algebraic equations is solved using the fully implicit Matlab solver ode15s.

We start from the equilibrium state of the system and increase the overpotential up to 200mV. The initial potential of the electrode is set to zero. We set the potential of zero charge to zero, $\Phi_{\text{pzc}} = 0$. In our simulation, we do not consider chemical interactions between electrolyte and electrode and have not incorporated chemical reactions. Furthermore, we neglect specific adsorption of ions at the electrode surface. This is in contrast to the experimental set-up, in which the initial state of the system is the OCP which might not be the potential of zero charge.

C Boundary conditions

We assume that the system is electro-neutral in the bulk electrolyte $\rho_F(x = L) = 0$ and in equilibrium with a reference electrode $\Phi(x = L) = 0$ and set the bulk values for charge density and electric potential to zero. At the electrified interface, no reaction is occurring and all fluxes are vanishing, i.e., $\mathbf{J}(x = 0) = 0$ and $\mathbf{v}(x = 0) = 0$. The electric potential in the electrolyte $\Phi(x = 0)$ is equal to the electrode potential.
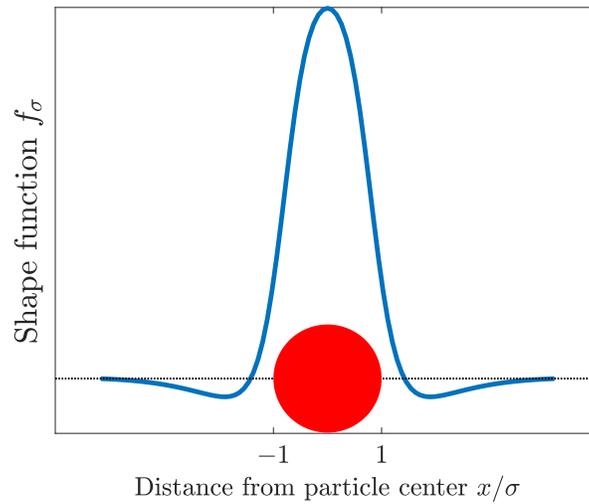
Fig. 1 Dimensionless shape function with indicated particle extension.

References

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