Cations Effect on Pt Electrodes in Alkaline HER Conditions Studied by Molecular Dynamics at Constant Potentials

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Rising interest for dihydrogen as an energy vector has been putting the hydrogen evolution reaction (HER) at the forefront of research. The HER has been highly studied and optimized at different scales: catalyst design, operating conditions (pH, temperature) and electrolyte. At the electrolyte level, the crucial role of the cations has been highlighted on Pt, hinting that their re-organization within the electrochemical double layer (EDL) may critically influence a given reaction kinetics [1]. A coherent mapping of the EDL structure can be obtained using "classical" molecular dynamics (MD) in order to rationalize this influence.

In 2020, the MetalWalls package [2] was developed in order to perform 'all-atom constant potential MD' and has been enabling a detailed mapping of the EDL. With the aim of unveiling the link between cations nature and the electrode/electrolyte properties, this study focuses on MD simulations at 0 and 1V on platinum monocrystalline facets. Different electrolytes (Aqueous solutions of 1M NaOH, KOH, CsOH) are investigated. Key properties such as the water distribution and its orientation as a function of the distance to the Pt surface as well as the cation concentration and their 1st shell solvation characteristics as a function of the distance to the Pt surface have been obtained, as illustrated in **Figure 1**, and the pivotal influence of the cation nature on these properties evidenced. The observed properties are then discussed in the light of experimental observations to correlate electrode/electrolyte interface properties and HER activity [3].

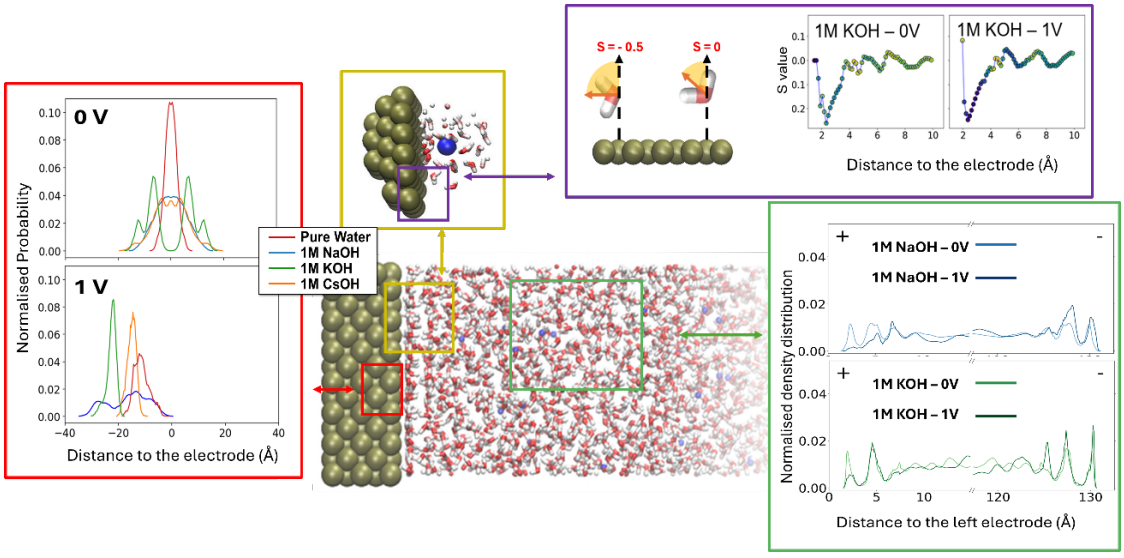

Figure 1 : Snapshot of the 1M NaOH system after 5 ns. Extracted data are presented as electrode charge for system with different cation types (red box), view of a solvated Na^+ near Pt(100) electrode (yellow box), orientation of water near the electrode measured through the orientation order parameters for K^+ systems (purple box), density profile of Na^+, and K^+ along the z axes of the box (green box). The simulation were performed at 0 and 1V during 10-20 ns in a box of 14nm long using the MetaWalls software.

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[3] A. Goyal *et al.*, *J Am Chem Soc*, 146, 7305–7312, (2024)