

Structural and Electrostatic Asymmetry at Charged Platinum–Nafion Thin-Film Interfaces Explored by MD Simulations

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Polymer electrolyte membrane fuel cells (PEMFCs) play a vital role in establishing a sustainable hydrogen economy, making research into their performance and durability an important endeavor. For the performance of PEMFCs, the cathode-catalyst layer (CCL) plays an important role. This layer consists of a mixture of a proton-conducting ionomer phase and platinum catalyst supported on carbon substrate. At the platinum surface, the oxygen reduction reaction (ORR) takes place forming water as the product. The ionomer phase controls the supply of protons to the catalyst surface, as required for the electrochemical reaction. These protons are transported through a thin water film at the ionomer-platinum interface [1,2]. The thin-film configuration of ionomer, water and catalyst impacts the transport of oxygen and protons and, thus, CCL performance [3]. Currently, Nafion is the most used ionomer in PEMFCs. However, their perfluorinated alkane backbone constitutes an environmental concern. Current efforts in the development of ionic polymers focus on identifying non-fluorinated replacements of Nafion with similar or even better performance and stability.

Using molecular dynamics simulations, we investigate the interface region between a platinum slab and a Nafion thin film, with a water layer in between, as depicted in Figure 1. By performing simulations with a charged platinum surface, we have calculated the electrostatic potential across the interface region, which we have used to define the effective electrode potential and to determine the differential capacitance of the charged interface (cf. Figure 2). The observed asymmetric behaviour in the differential capacitance is opposite to the expectation, and was rationalized by tracking the changes of the hydronium ions adsorbed to the surface w.r.t. the different surface charges. The favourable water content was estimated by evaluating the energy differences between systems with varying amounts of water. These complementary analyses yield vital insights into the microscopic interface region formed by catalyst, water and ionomer, which is inaccessible for experiment.

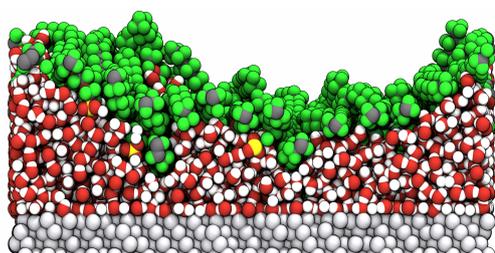


Figure 1: Exemplary snapshot of one of the investigated systems of a water layer confined by a platinum slab on the one side, and a Nafion thin film on the other. Color code: H: white; C: black; O: red; F: green; S: yellow.

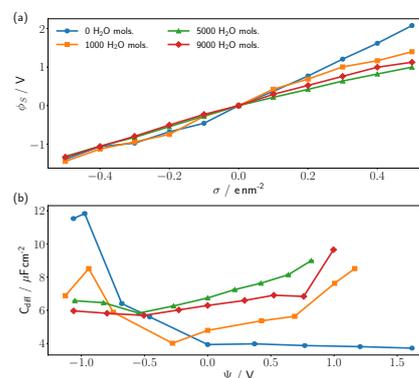


Figure 2: (a) Electric surface potentials ϕ_s per surface charge for each water content. Offset so that the uncharged systems have $\phi_s=0$. (b) Differential capacitance C_{diff} per electric surface potential for each water content.

- [1] F. Chabot, *et al.*, ACS Appl. Energy Mater. **2023**, 6, 1185–1196.
- [2] F. Chabot, *et al.*, J. Electrochem. Soc. **2024**, 171, 124506.
- [3] W. Olbrich, *et al.*, J. Electrochem. Soc., **2022**, 169, 054521.