

## SUPPORT MATERIAL

### What is the Trigger for Hydrogen Evolution Reaction? – Towards Electrocatalysis Beyond the Sabatier Principle

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**\*Why ice-like structure could exist at  $E_{pzc}$**  – The following discussion is taken from reference [1]. By the formal definition the Galvani potential ( $\phi$ ) for one phase (metal or electrolyte) in contact with vacuum is the sum of the surface potential ( $\chi$ ) and the Volta (outer) potential ( $\psi$ ) so the Galvani potential difference should be<sup>[1]</sup>:

$$\Delta_S^M \phi = \phi_M - \phi_S = \Delta_S^M \chi + \Delta_S^M \psi \quad \text{Equation S1}$$

However, when an interface is created between two phases, surface potentials (the electrostatic work to transport the charged species through the dipole layer of the surface) are modified for the phase interactions. Namely, the surface potential of the metal is changed due to the interaction with the liquid phase:

$$g_{(S)}^M(dip) = \chi_M + \delta\chi_{(S)}^M \quad \text{Equation S2}$$

At the same time the surface potential of the electrolyte is altered due to interaction with the solid phase:

$$g_{(M)}^S(dip) = \chi_S + \delta\chi_{(M)}^S \quad \text{Equation S3}$$

Consequently, the potential drop at the interface induced by the altered surface potentials of two phases will be:

$$g_S^M(dip) = g_{(S)}^M(dip) - g_{(M)}^S(dip) \quad \text{Equation S4}$$

Besides the altered surface potentials, another contributor to the electric potential drop between the two phases is the charge separation in the double layer. That is in fact the contribution of the ions in the double layer ( $g_S^M(ion)$ ) to the overall Galvani potential difference between the two

phases. Consequently, the Galvani potential difference between the bulk of the solid and the bulk of the liquid will be the sum of ionic and dipole contributions:

$$\Delta_S^M \phi = g_S^M(ion) + g_S^M(dip) \quad \text{Equation S5}$$

When we combine Eq.S1-S5 we get:

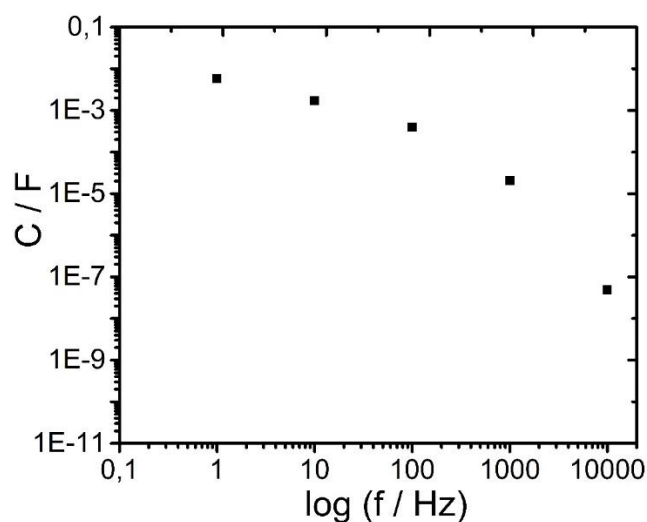
$$\Delta_S^M \phi = \Delta_S^M \chi + \Delta_S^M \psi = g_S^M(ion) + F\chi_M + F\delta\chi_{(S)}^M - F\chi_S - F\delta\chi_{(M)}^S \quad \text{Equation S6}$$

From Eq.S1-S6 it seems that  $\Delta_S^M \psi = g_S^M(ion) + F\delta\chi_{(S)}^M - F\delta\chi_{(M)}^S$ . At the potential of zero charge ( $E_{pzc}$ ) there is no charge separation in the double layer ( $g_S^M(ion) = 0$ ). However, the Volta potential (equivalent to the potential drop from the infinity point in the vacuum to a position just outside the surface of the phase) difference remains and equals to  $F\delta\chi_{(S)}^M - F\delta\chi_{(M)}^S$ . So, at the potential of zero charge, the Galvani potential difference between the bulk of the metal and the bulk of the electrolyte still exists as shown with Eq.7:

$$\Delta_S^M \phi = \Delta_S^M \chi + \Delta_S^M \psi = F\chi_M - F\chi_S + F\delta\chi_{(S)}^M - F\delta\chi_{(M)}^S \quad \text{Equation S7}$$

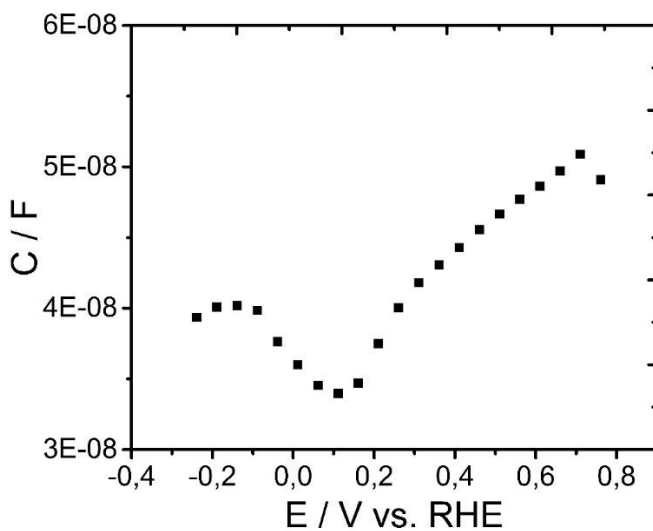
Existence of ice-like structure at  $E_{pzc}$  should be proven experimentally, however, it is evident from Eq.7 that the Galvani potential difference, originating in altered surface potentials of both phases, exists at  $E_{pzc}$ . Therefore, the configuration of surface water layer will differ from bulk water.

### **\*Frequency dependence of total capacitance**



**S.1.** Dependence of the total capacitance from the AC frequency on Pt-poly at open circuit potential in 0.1 M HClO<sub>4</sub>

**\*Influence of high concentration of anions on E<sub>pme</sub>**



**S.2;** Total capacitance of Pt-poly in 0.1 M HClO<sub>4</sub> monitored using electrochemical impedance spectroscopy in Mott-Schottky operational mode as a function of applied potential using linear sweep with imposed sinusoidal perturbation recorded at a frequency of at least 10000 Hz with a potential step of 50 mV

## REFERENCES:

- [1] S. Trasatti, R. Parsons, *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *205*, 359–376.