The influence of non-covalent interactions on the hydrogen peroxide electrochemistry on platinum in alkaline electrolytes

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Supporting information

Experimental Section

A Teflon three-compartment electrochemical cell was used for the measurements. The experiments were performed at room temperature using a rotating disc electrode setup, a Gamry Reference 600 potentiostat and a Radiometer Analytical rotation controller. All components were automatically controlled and programmed using in-house-built LabVIEW software [1]. The working electrode was a polycrystalline Pt disc (geometrical area: 0.196 cm^2), embedded in a Teflon cylinder and polished with a silica suspension (final polishing suspension: 0.1 μm, Buehler; polishing cloth: Struers, MD Chem) prior to the measurements. The counter electrode was a platinum wire for the cyclic voltammetric investigations and a graphite rod for the electrolysis experiments. The reference electrode was a saturated Ag/AgCl electrode (Metrohm), however all potentials are expressed with respect to the reversible hydrogen electrode (RHE) potential. The counter and the reference electrodes were separated from the main compartment with a Nafion membrane [2]. Positive feedback was used for compensating for the electrolyte resistance; the residual uncompensated resistance was less than 2 Ω in all experiments. All solutions were freshly prepared using ultrapure water (18 MΩ, TOC < 3 ppb, ELGA®) and super-pure chemicals (Merck, suprapure®). The gases were provided by Air Liquide (99.999 % purity).

Negative-going sweep of the cyclic voltammograms in alkaline electrolyte

Figure S1 shows the cyclic voltammograms that were recorded in 0.1 M alkaline electrolyte (MOH) of different alkali metal cation (M^+: Li^+, Na^+ or K^+) as well as the corresponding cyclic voltammograms in 0.1 M $HClO_4$. Figure S1(b) and (c) show background-corrected responses. The positive-going sweep of Fig. S1(b) and (c), which was presented in the Fig. 1 of the main text, is shown here with faint color while the strongly colored curves show the negative-going sweeps.
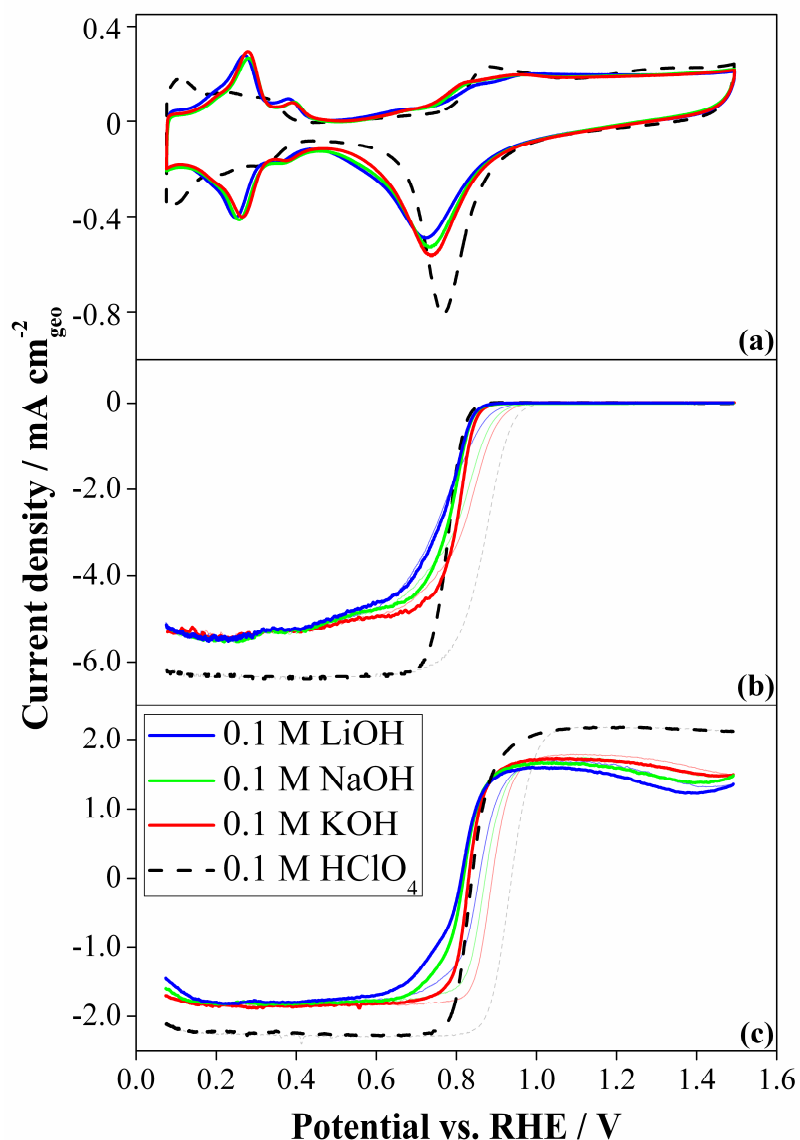
Figure S1. Hydrodynamic voltammograms on polycrystalline Pt in $HClO_4$ and in alkaline electrolytes containing different alkali metal cations. CVs recorded in (a) Argon-saturated solutions (b) Oxygen-saturated solutions (c) Argon saturated solutions containing 1×10^{-3} M H_2O_2. Scan rate: 0.1 V s^{-1}, Rotation rate: 1600 rpm. Background-corrected sweeps in (b) and (c) are shown. The curves with faint color in (b) and (c) represent the positive-going sweep (identical to the Fig. 1 of the main text) while the strongly colored curves represent the negative-going sweep.

Determination of the ORR-corrected mixed potential (c-MP)

The definition of the ORR-corrected mixed potential (c-MP) was given in Ref. [3]. In order to determine the c-MP, cyclic voltammograms in H_2O_2–containing solution must be recorded at different rotation rates and the c-MP is the potential at which the positive-going sweeps coincide for all rotation rates. In Fig. S2 we show an example of the determination of the c-MP for one measurement in 0.1 M KOH.

Ideally, the crossing point of all positive-going sweeps should be clearly at zero current. However, in the transition region hydrogen peroxide is partially oxidized producing oxygen, which can be reduced at these potentials shifting the crossing point downwards.
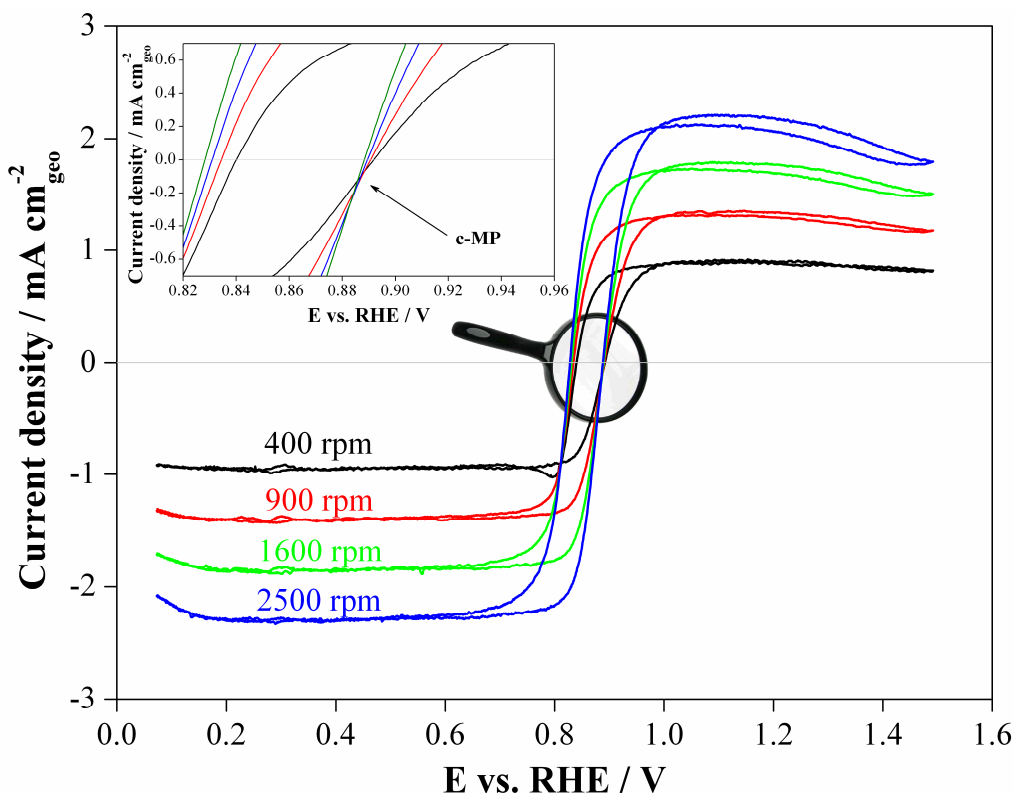
Figure S2. Background-corrected hydrodynamic voltammograms on polycrystalline Pt in 0.1 M KOH + 1x10^{-3} M H$_2$O$_2$ recorded under Argon atmosphere at different rotation rates. Scan rate: 0.1 V s^{-1}. The inset is an enlarged picture of the region close to the c-MP.

The crossing point is not always clearly identified from the cyclic voltammograms, as it can also be seen in the inset of Fig. S2, where the CV at 400 rpm slightly declines from the crossing point of the other sweeps, which is a reproducible observation. Even though all curves cross each other in a potential range of 2 mV, we preferred to use an objective method to determine the c-MP. Therefore an objective function was used which includes the sum of the squared differences between the current responses of each measurement:

$$S(E) = [i_{400}(E) - i_{900}(E)]^2 + [i_{400}(E) - i_{1600}(E)]^2 + [i_{400}(E) - i_{2500}(E)]^2 +$$
$$+ [i_{900}(E) - i_{1600}(E)]^2 + [i_{900}(E) - i_{2500}(E)]^2 + [i_{1600}(E) - i_{2500}(E)]^2$$

where i$_x$(E) is the current measured at *x* rotation rate. The potential at which the objective function is minimized is the ORR-corrected mixed potential. It should be noted that the value of the objective function at the c-MP should ideally be zero, but it was typically in the order of 10^{-11} A^2.

Cyclic voltammograms in 0.1 M CsOH electrolyte

Figure S3 shows the positive-going sweeps of the voltammograms shown in Fig. 1c of the main text, together with that in 0.1 M CsOH electrolyte. The CV in 0.1 M CsOH is not following the trend in the transition region, as it would be expected from the lower hydration

energy of Cs^+ compared to K^+. The reason for this inconsistency is discussed in the text. However, it is worth mentioning that the decrease of the current in the H_{upd} region and in the irreversible "oxide" region is in both cases less pronounced compared to all other cations, showing that the inhibiting effect becomes weaker in the order $Li^+ > Na^+ > K^+ > Cs^+$.
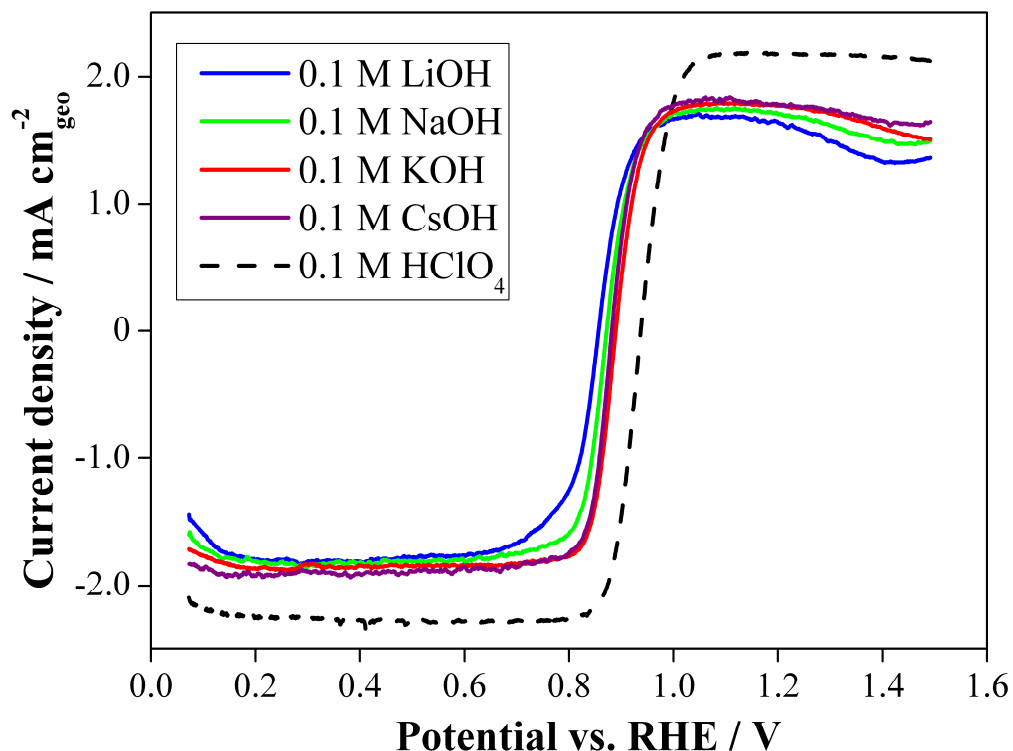

Figure S3. Positive-going background-corrected hydrodynamic voltammograms on polycrystalline Pt in 0.1 M MOH + 1×10^{-3} M H_2O_2 recorded under Argon atmosphere. M^+: Li^+, Na^+, K^+, Cs^+. The CV in 0.1 M $HClO_4$ is also shown for comparison. Scan rate: 0.1 V s^{-1}. Rotation rate: 1600 rpm.

References

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