Supporting Information
The Subtle Helpers: How Spectator Ions Govern Efficiency in Electrolytic Water Splitting

Supplementary Note 1: Calculation of the Tafel slope for hydrogen evolution reaction.[1]

According to the IUPAC Technical Report， the Tafel slope is defined as follows: The Tafel slope is a fundamental parameter in electrode reaction kinetics, defined as: Cathodic Tafel slope: $\alpha_c = -(RT/F)(d\ln|j_c|/dE)$; Anodic Tafel slope: $\alpha_a = (RT/F)(d\ln j_a/dE)$. In hydrogen evolution reaction (HER) studies, we primarily focus on the cathodic Tafel slope.

HER: $\alpha_c = n_f / \nu + n_r\beta$

n_f is the number of electrons released by the electrode before the rds

ν is the number of occurrences of the rds in the electrode reaction as written

n_r is the number of electrons involved in the rds

β is the symmetry factor, which is usually assumed to take values close to 0.5

$b = 2.303RT / \alpha_c nF = 59.2/\alpha_c$ (rds:n=1)

Volmer : $H^+ + e^- \rightarrow H_{ads}$

Tafel : $2H_{ads} \rightarrow H_2$

Heyrovsky : $H_{ads} + H^+ + e^- \rightarrow H_2$

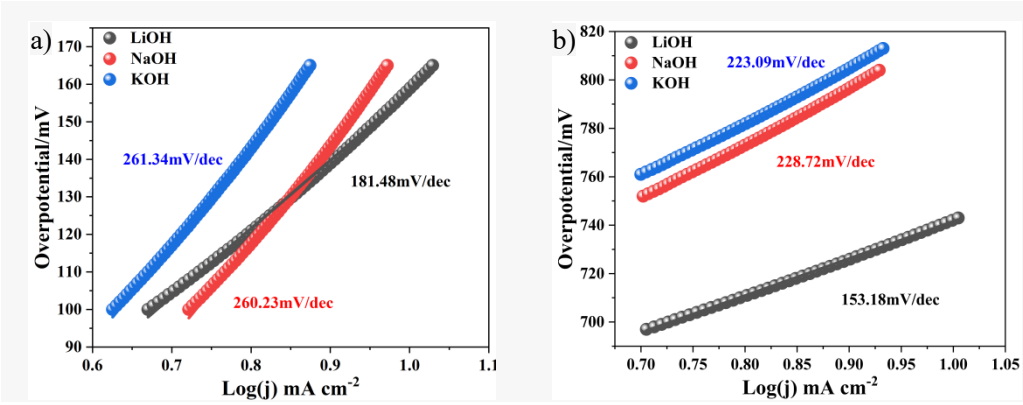
The hydrogen evolution reaction (HER) proceeds through distinct pathways depending on the electrolyte environment: In acidic conditions, the initial step involves proton adsorption (M-H^+), while in neutral or alkaline environments, water molecule/proton adsorption (M-HOH) occurs, followed by reduction to form M-H* (with concomitant OH^- release in the case of chemisorbed water reduction). From this M-H* intermediate, two distinct mechanistic pathways emerge: (1) The Tafel step involves combination of two chemisorbed H* species (H_{ad}), leading to chemical desorption of $H_{2,ad}$ (Volmer-Tafel mechanism); or (2) The Heyrovsky step features electrochemical reaction between chemisorbed H* and solution-phase protons/water molecules, resulting in electrochemical desorption of H_2 (Volmer-Heyrovsky mechanism). These pathways exemplify the multistep nature of electrode processes discussed in the IUPAC report, where proper identification of rate-determining steps (whether chemical or electrochemical) is crucial for accurate kinetic analysis. We will calculate the Tafel slopes for the HER separately according to the Volmer-Tafel and Volmer-Heyrovsky mechanisms.

1. Volmer-Tafel

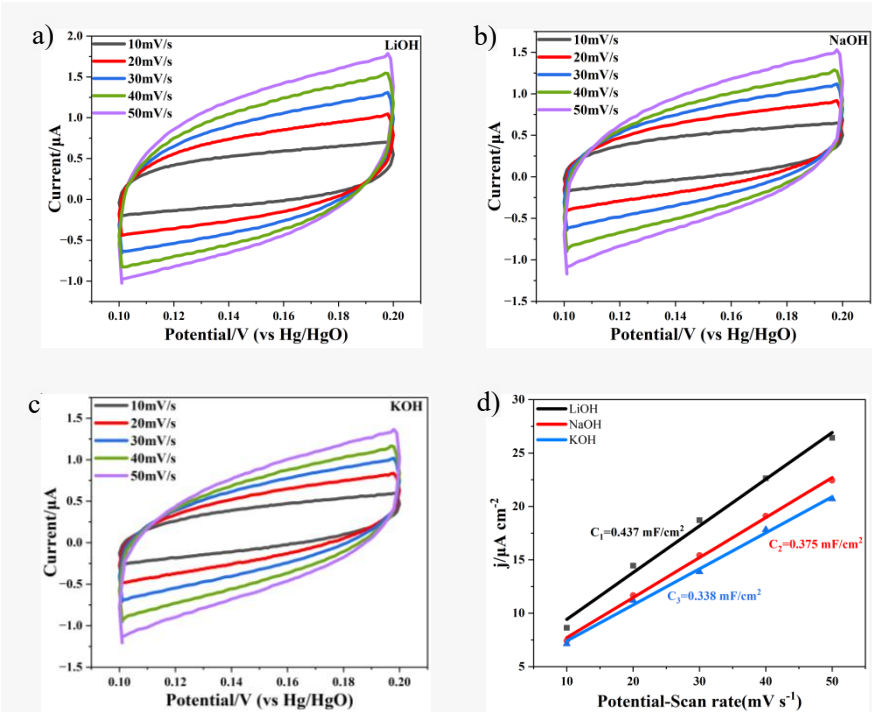
rds	n_f	ν	n_r	β	α_c	b(mV/dec)
Volmer	0	2	1	0.5	0.5	118.4
Tafel	2	1	0	0.5	2	29.6

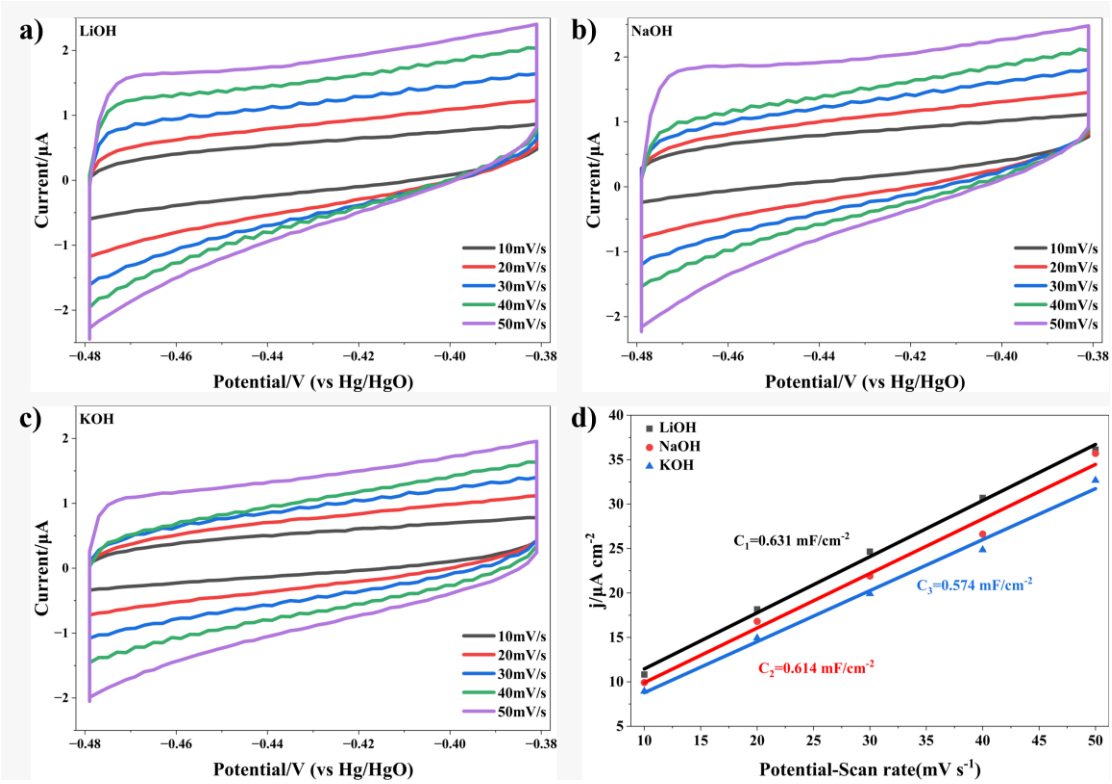
2. Volmer-Heyrovsky

Rds	n_f	ν	n_r	β	α_c	b(mV/dec)
Volmer	0	2	1	0.5	0.5	118.4
Heyrovsky	1	1	1	0.5	1.5	39.5



Supplementary Figure 1. The Tafel slopes (a and b) of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) of platinum electrodes in LiOH, NaOH and KOH solutions (pH=12.6) vs RHE.

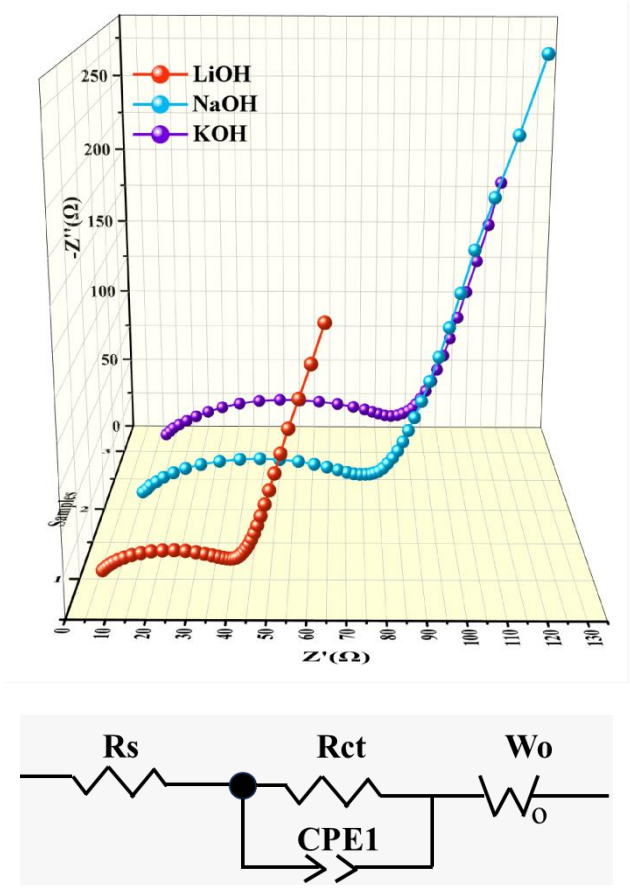




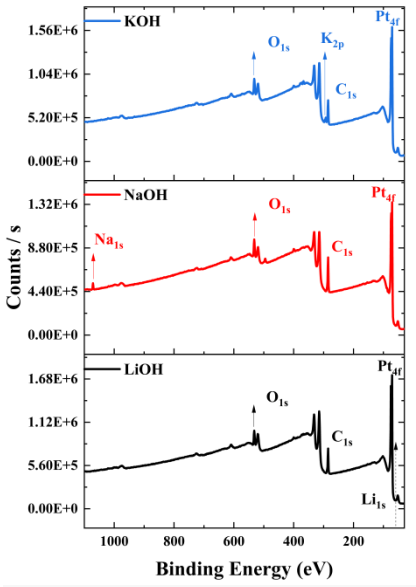
Supplementary Figure 2. Electric double layer capacitance (EDLC) in MOH (M = Li^+, Na^+, and K^+) solutions. EDLC data of platinum disc electrodes in the three solutions at pH 12.6. Color coded: LOH: black, NaOH: red, and KOH: blue.

The electrochemical active surface area (ECSA) was calculated using the following equation: ECSA = Cdl/Cs

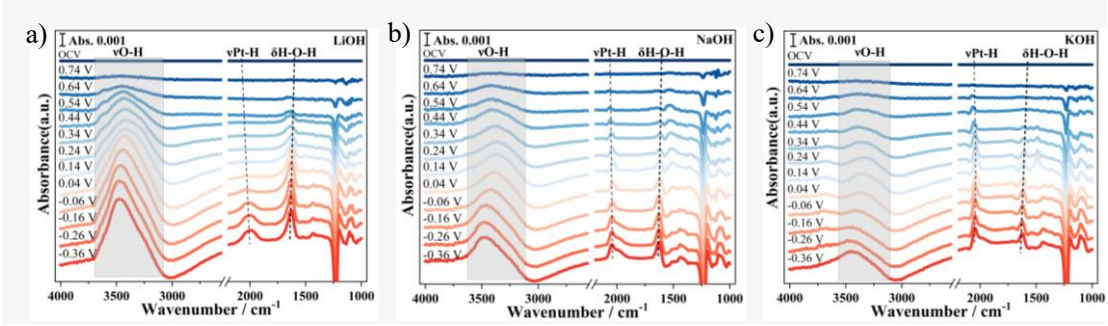
where Cdl represents the double-layer capacitance and Cs is the specific capacitance of the material (typically 0.04 mF cm^{-2}). The double-layer capacitance (Cdl) was determined by collecting cyclic voltammograms at various scan rates in the non-Faradaic region (0.10 V to 0.20 V vs. Hg/HgO). Specifically, the Cdl value was obtained from the slope of the linear plot of the half-current density difference Δj (Δj = (ja - jc)/2, where ja and jc represent the anodic and cathodic current densities, respectively versus scan rate.



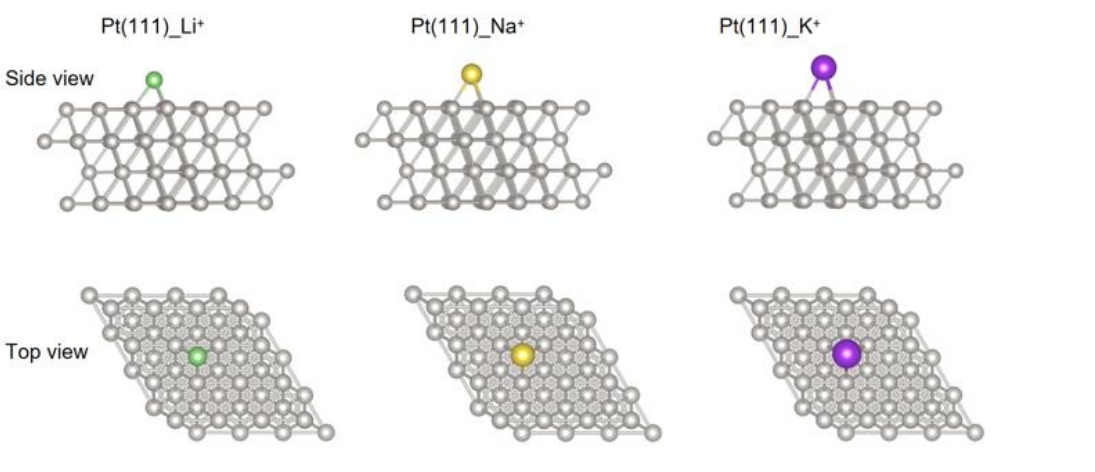
Supplementary Figure 3. Impedance spectra of MOH (M = Li+, Na+, and K+) solutions. Impedance data of platinum disc electrodes in the three solutions at pH 12.6. Color coded: LOH: red, NaOH: blue, and KOH: purple.



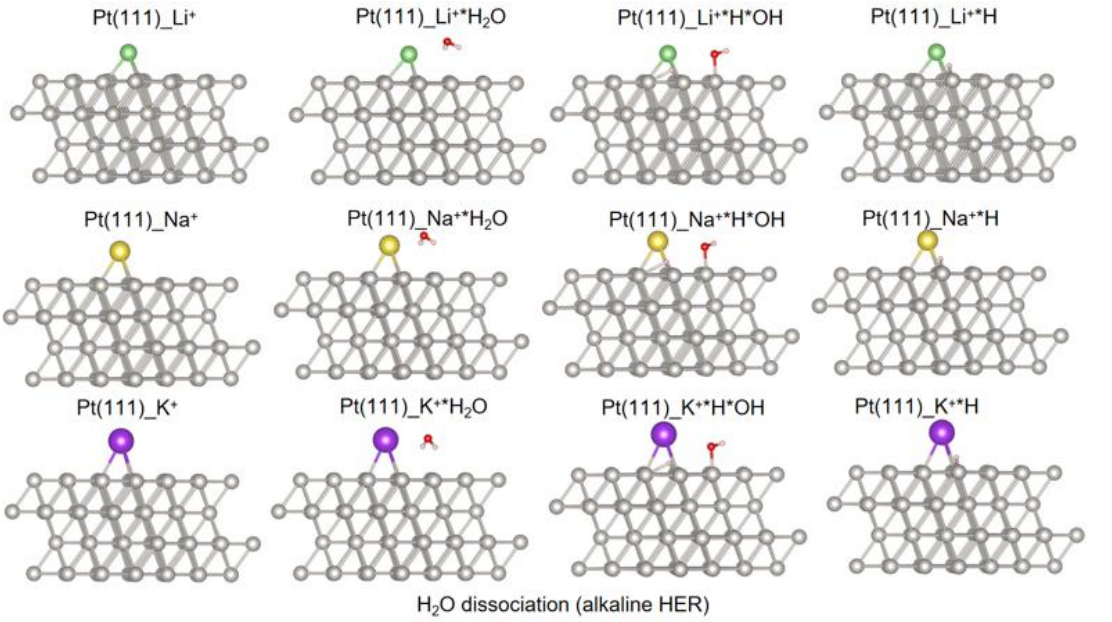
Supplementary Figure 4. X-ray photoelectron spectroscopy (XPS) of Pt electrode at potential -0.36 V (vs RHE) for 10 min **in three pH=12.6 electrolytes, LiOH, NaOH and KOH.**



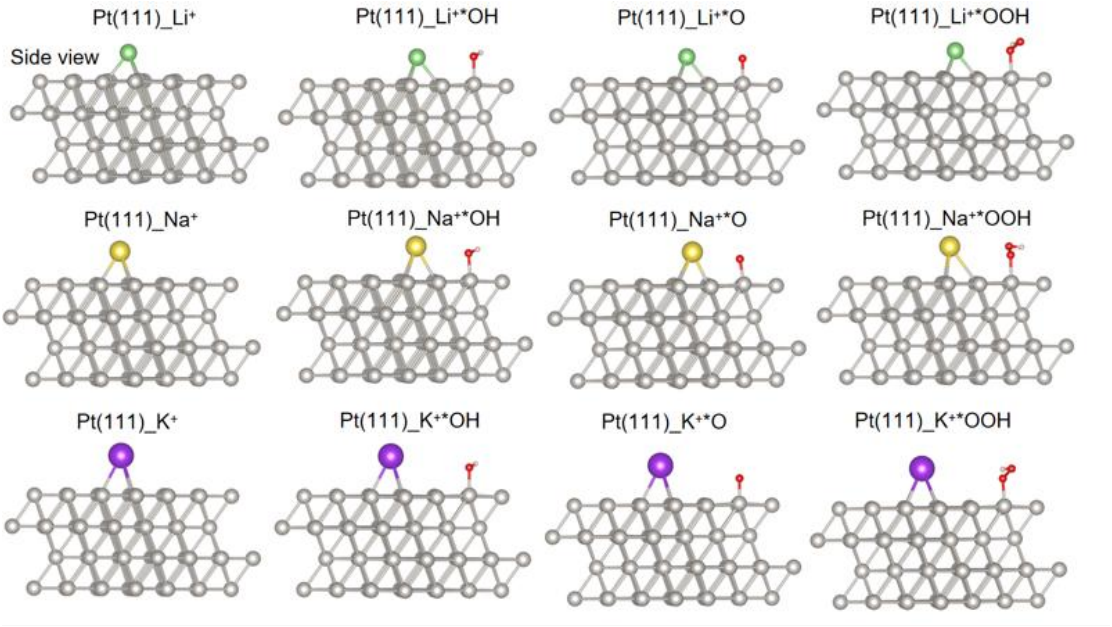
Supplementary Figure 5. Dynamic reaction investigation using in situ ATR-FTIRS (Fourier-transform infrared spectroscopy) for hydrogen evolution reduction. In situ ATR-FTIRS recorded for platinum (Pt) electrodes in LiOH(a), NaOH(b), and KOH(c) electrolyte from open circuit voltage to -0.15 V (vs RHE).



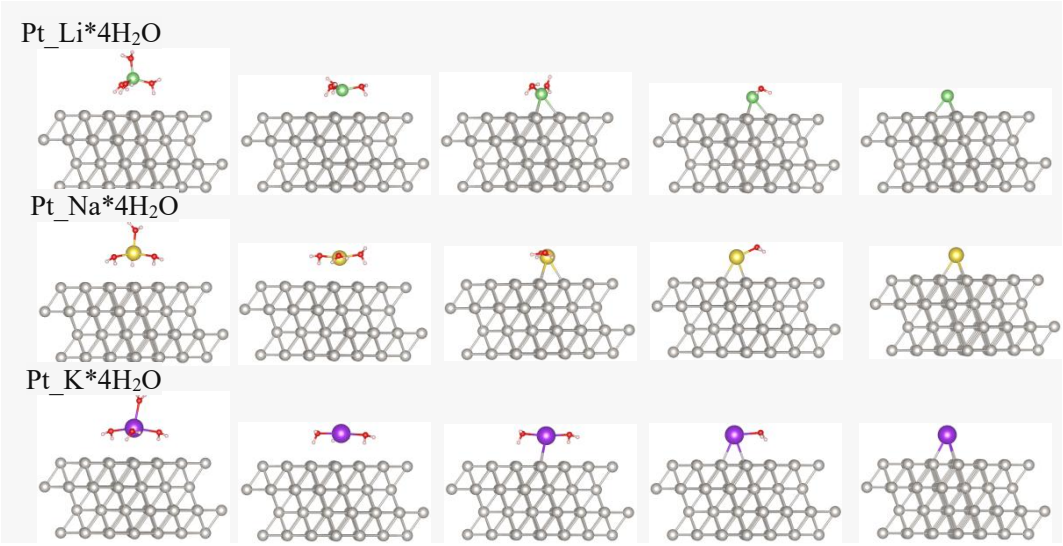
Supplementary Figure 6. Cations adsorption modeling on Pt(111) surface. The most stable adsorption configurations of cations on Pt(111) surface. Color coded: Li: green, Na: yellow, and K: purple.



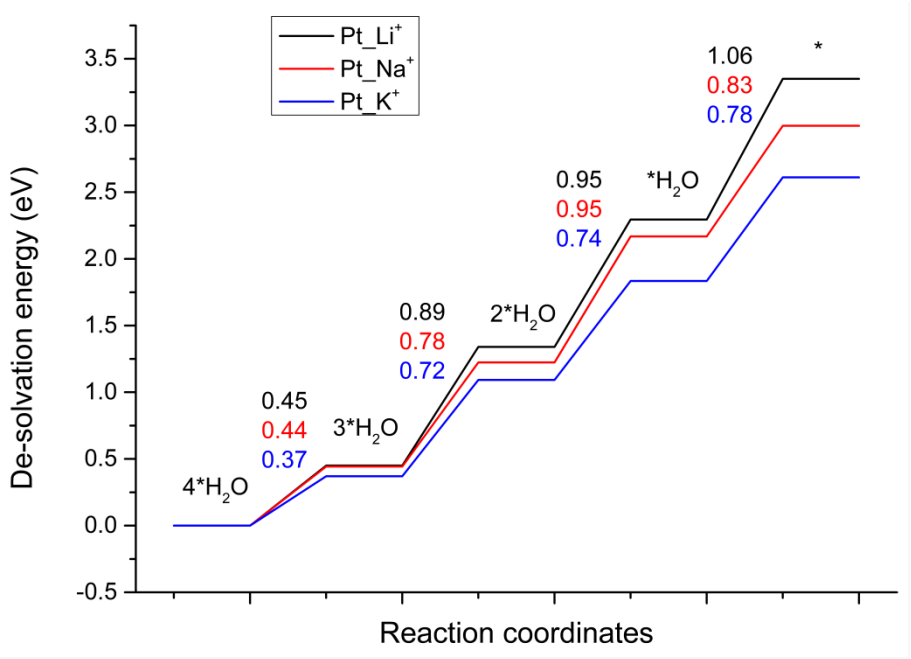
Supplementary Figure 7. Adsorption model of the Volmer step occurring in the presence of cations (Li^+, Na^+, and K^+). In the presence of cations, the Volmer step ($H_2O + e^- + * \rightarrow H^* + OH^-$) occurs, and H_2O, *H, and *OH adsorb on the Pt(111) surface. Color coded: O: red, H: white, Li: green, Na: yellow, and K: purple.



Supplementary Figure 8. Adsorption modeling of intermediates in the presence of cations (Li^+, Na^+, and K^+). Adsorption configurations of cations and *H, *OH, *O, and *OOH adsorbed on the Pt(111) surface. Color coded: O: red, H: white, Li: green, Na: yellow, and K: purple.



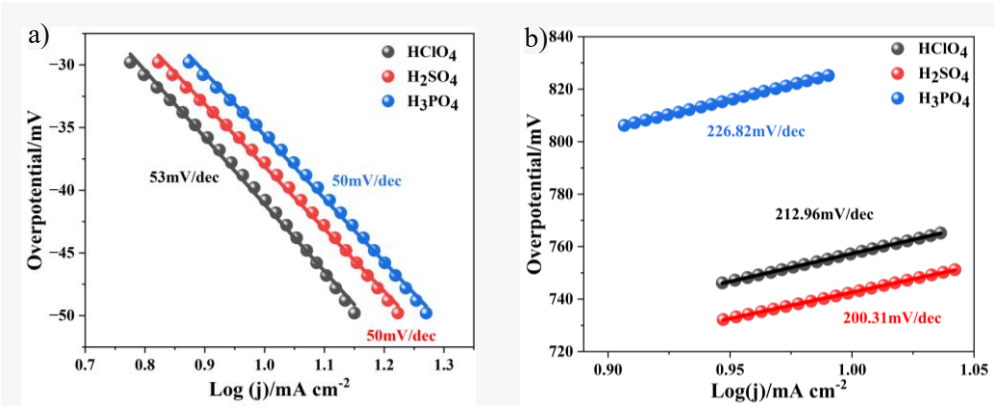
Supplementary Figure 9. Adsorption model of the dehydration process of hydrated cations (Li^+, Na^+, and K^+). Tetrahydrated cations are sequentially dehydrated to expose cations adsorbed on the Pt(111) surface.



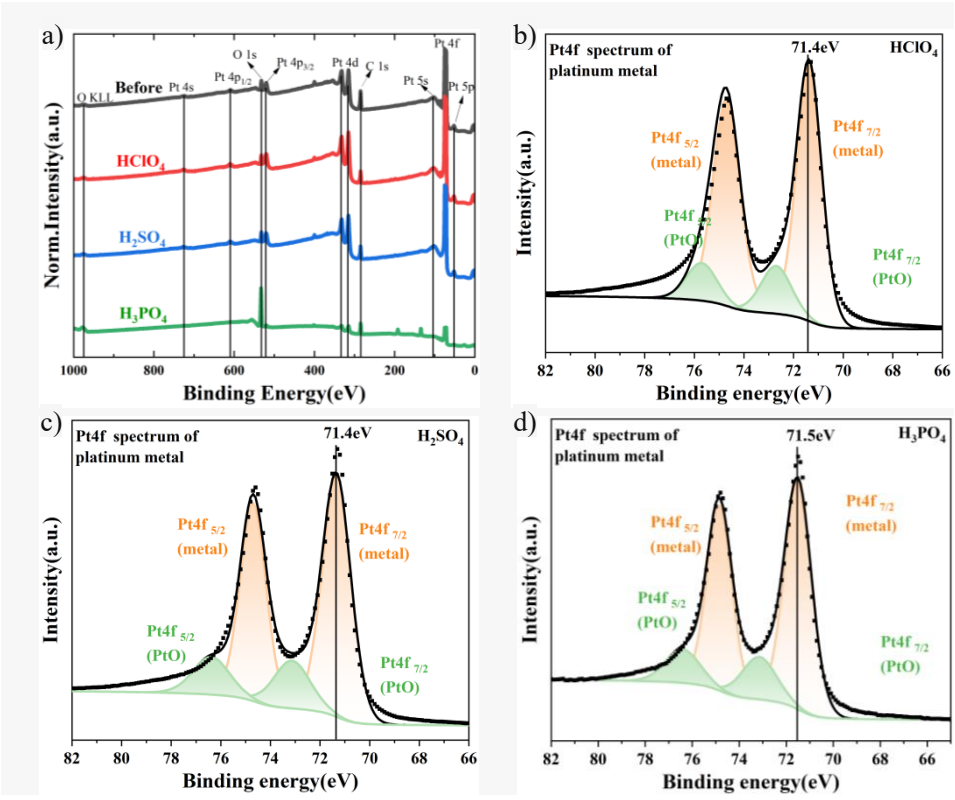
Supplementary Figure 10. Dehydration capacity of hydrated cations. The dehydration energy of cations (Li^+, Na^+, and K^+) from carrying four water molecules to independent cations. Color coded: Li: black, Na: red, and K: blue.

We investigated the dehydration potential of hydrated cations. Due to the presence of negative charges on the electrode surface and hydrogen bonds in the solution, cations may be promoted to desolvation and adsorbed onto the Pt surface. Therefore, our model is based on the premise that this process occurs smoothly. From the reaction coordinate,

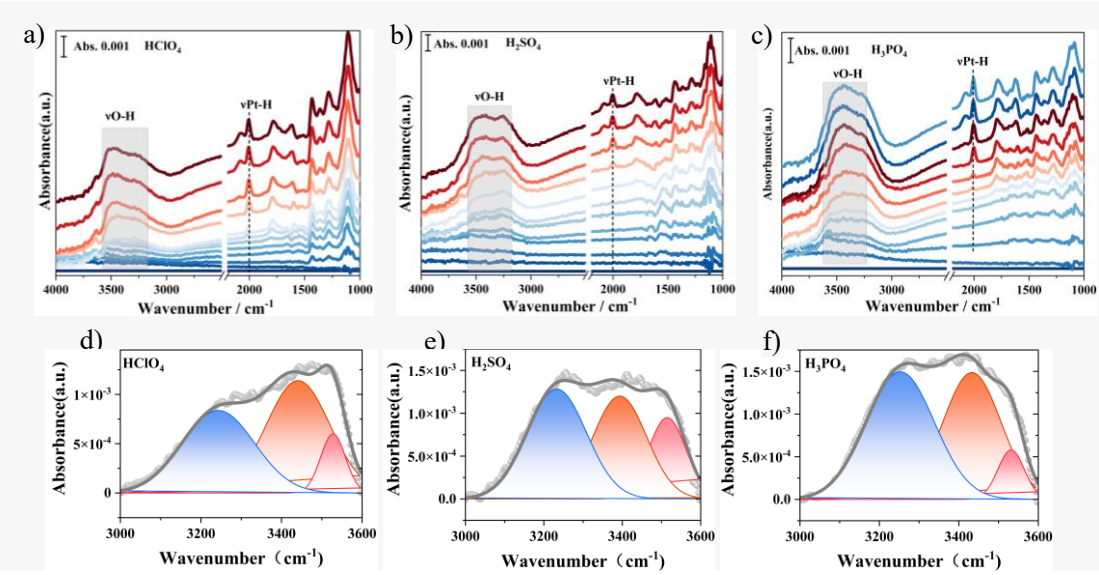
it can be seen that the corresponding energy requirement for cation dehydration is moderate and can be considered feasible.



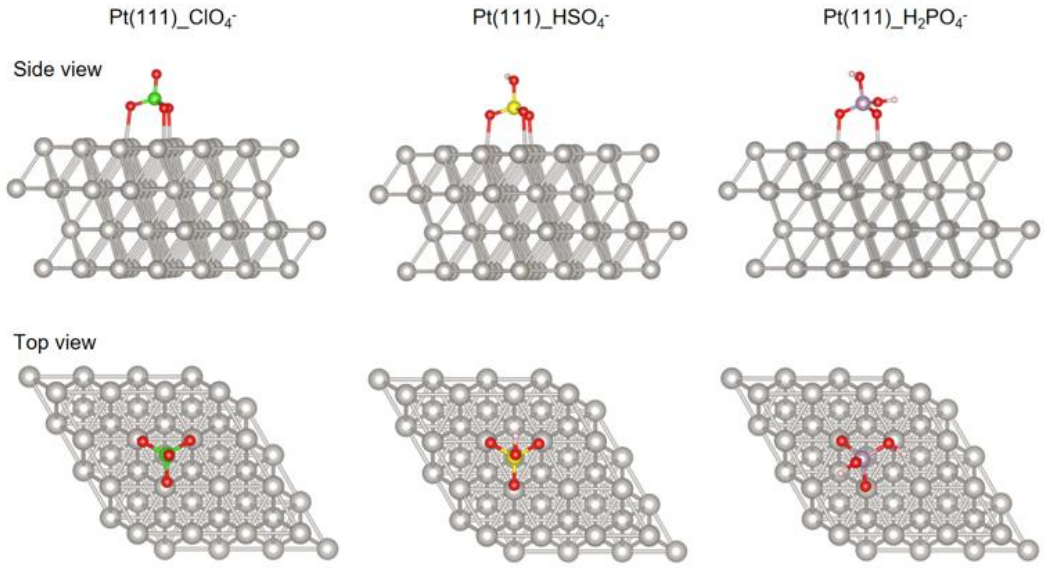
Supplementary Figure 11. The Tafel slopes (a and b) of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) of platinum electrodes in $HClO_4$, H_2SO_4 and H_3PO_4 solutions (pH=1.00) vs RHE.



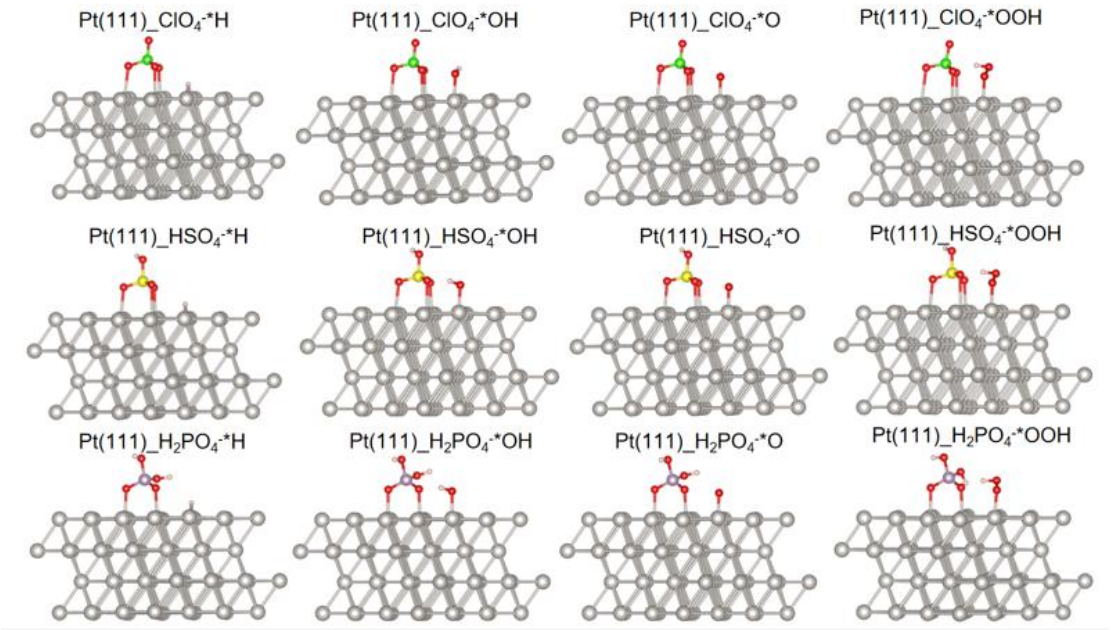
Supplementary Figure 12. The X-ray photoelectron spectroscopy (XPS) of Pt electrode at potential -1.2 V (vs Hg/HgO) for 10 min **a) - d)** in three pH=1.00 electrolytes, $HClO_4$, H_2SO_4 and H_3PO_4.



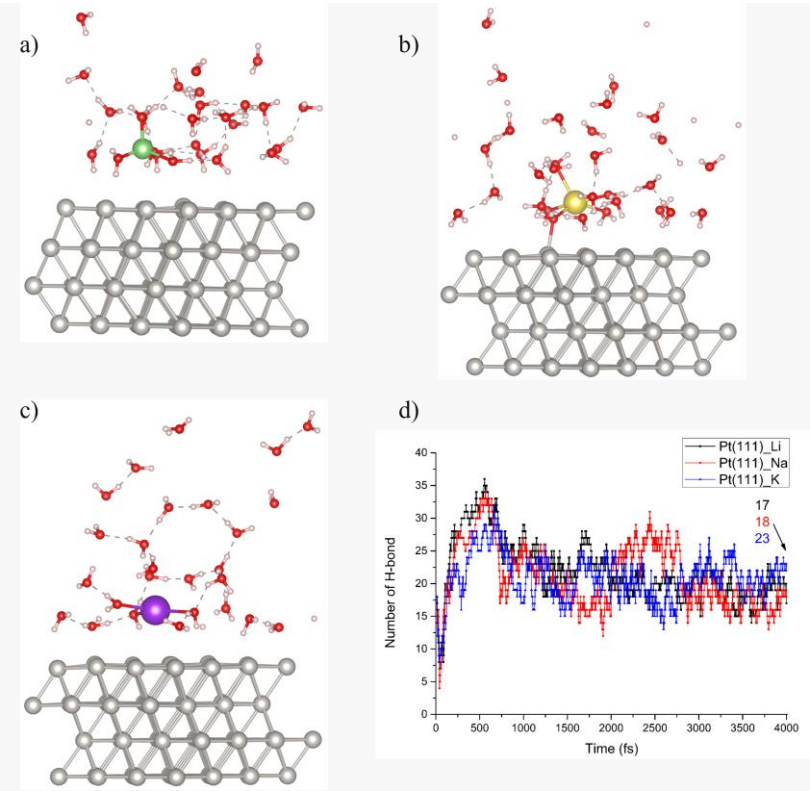
Supplementary Figure 13. Dynamic reaction investigation using in situ ATR-FTIRS (Fourier-transform infrared spectroscopy) for hydrogen evolution reduction. In situ ATR-FTIRS recorded for platinum (Pt) electrodes in $HClO_4$(a), H_2SO_4(b), and H_3PO_4(c) electrolyte from open circuit voltage to -0.15 V (vs RHE). d) - f) The νO-H peak at 3000 cm^{-1} to 3600 cm^{-1} under -0.15 V (vs RHE) conditions.

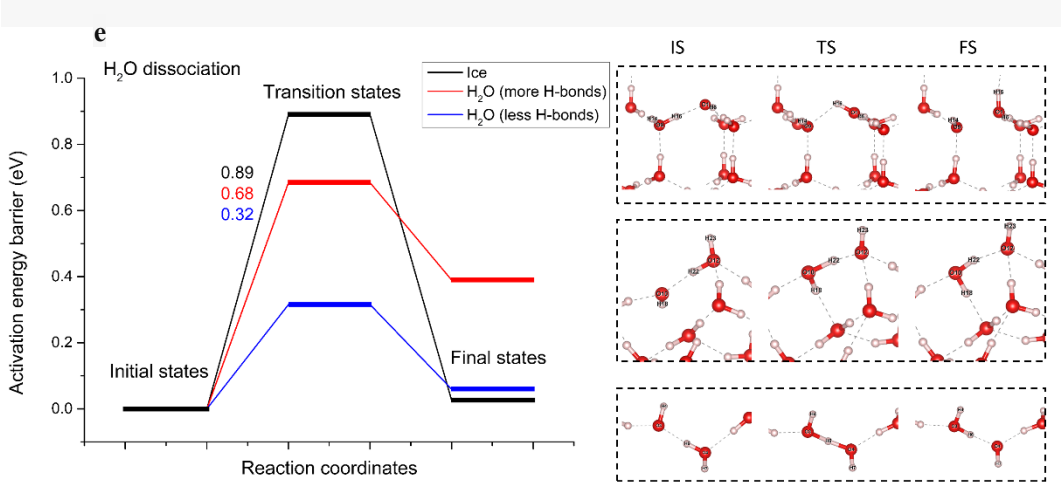


Supplementary Figure 14. Anion adsorption modeling on Pt(111) surface. The most stable adsorption configurations of anions on Pt(111) surface. Color coded: O: red, H: white, Cl: green, S: yellow, and P: purple.

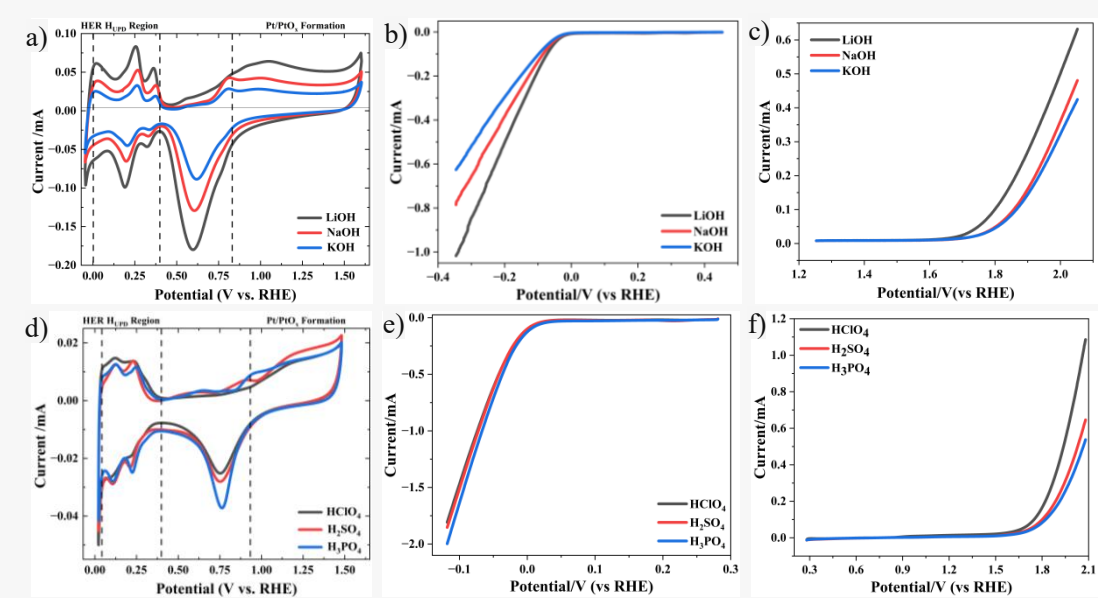


Supplementary Figure 15. Adsorption modeling of intermediates in the presence of anions. Adsorption configurations of anions and *H, *OH, *O, and *OOH adsorbed on the Pt(111) surface. Color coded: O: red, H: white, Cl: green, S: yellow, and P: purple.

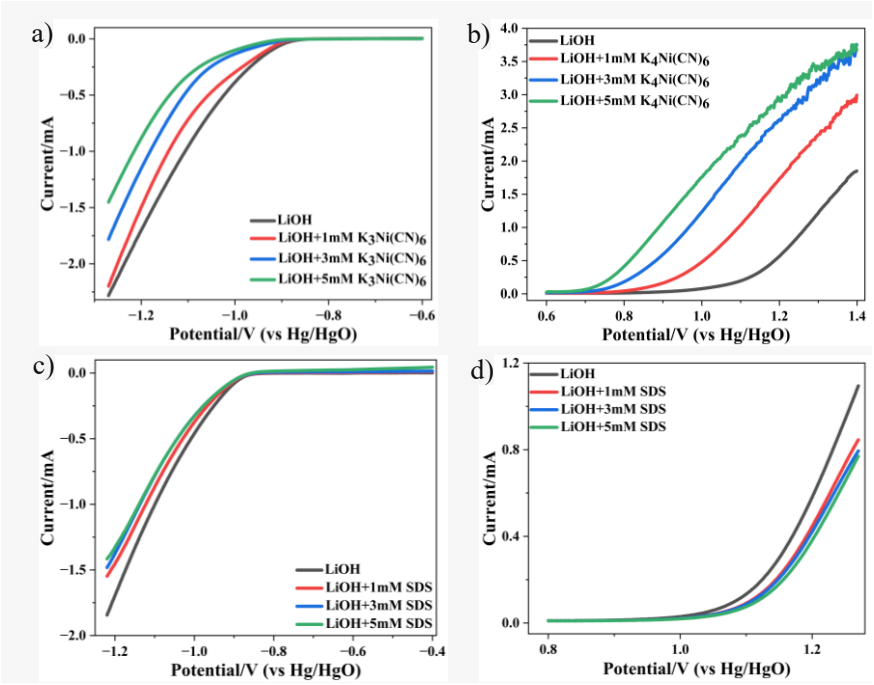




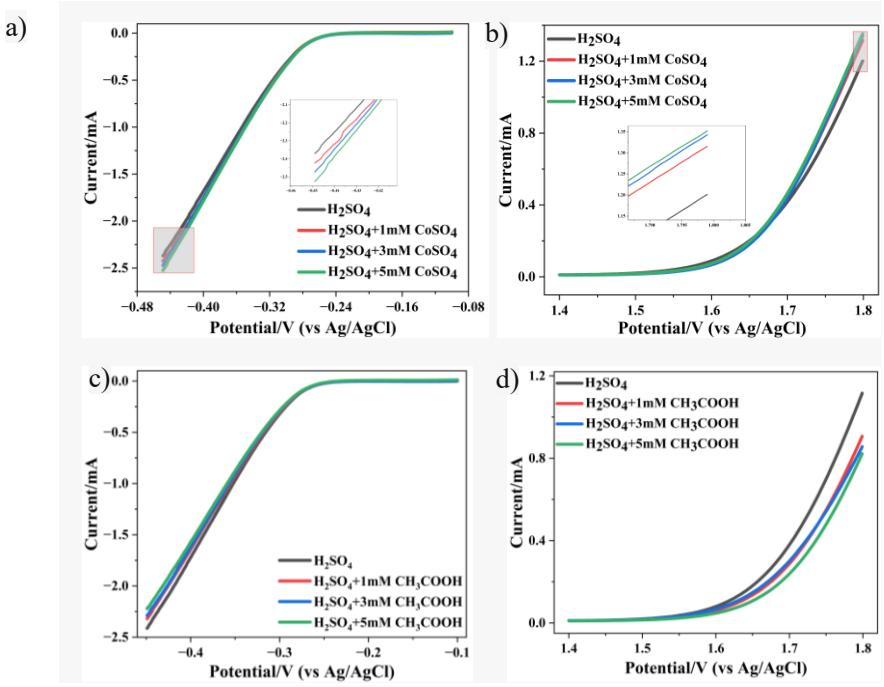
Supplementary Figure 16. a-c) the H-bond network of Pt(111)_Li, Pt(111)_Na and Pt(111)_K after 4000 fs AIMD simulation, the d) total H-bond number along the reaction coordinates of AIMD simulation, and the activation barriers of H_2O dissociation (e) under most ordered H-bond, more ordered H-bond, and less ordered H-bond.



Supplementary Figure 17. Characterization of the electrochemical behavior of platinum nanoparticles (Pt NPs). a) Characteristic Pt NPs cyclic voltammogram in three pH=12.6 electrolytes, LiOH, NaOH, and KOH. LSV curves for b) HER and c) OER in LiOH, NaOH, and KOH. d) Characteristic Pt NPs cyclic voltammogram in three pH=1.00 electrolytes, $HClO_4$, H_2SO_4, and H_3PO_4. LSV curves for b) HER and c) OER in $HClO_4$, H_2SO_4, and H_3PO_4.



Supplementary Figure 18. The effect of the addition of ions on hydrogen evolution reactions and oxygen evolution reactions in an alkaline environment.



Supplementary Figure 19. The effect of the addition of ions on hydrogen evolution reactions and oxygen evolution reactions in an acidic environment.

REFERENCES

[1] Guidelli, Rolando., Compton, Richard G., Feliu, Juan M., et.al. Defining the transfer coefficient in electrochemistry: An assessment (IUPAC Technical Report). Pure and Applied Chemistry, vol. 86, no. 2, 2014, pp. 245-258.