

The Cationic Enhancement Effect on the Two-Electron Oxygen Reduction Reaction in Acidic Conditions at Carbon-Based Cathodes

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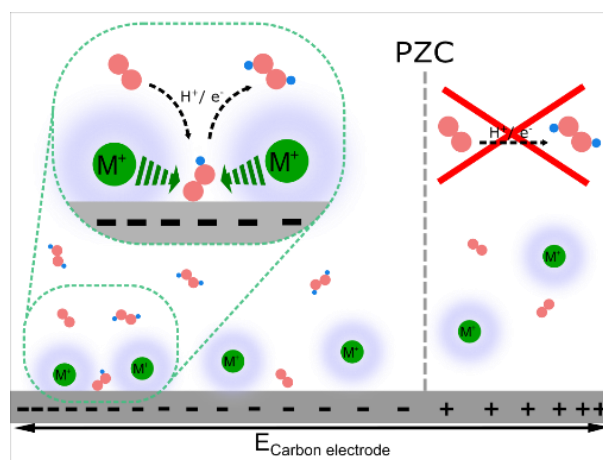
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Abstract

Hydrogen peroxide (H_2O_2) is a green oxidant, widely used in industry. To turn its synthesis green, research focused on the development of efficient catalysts for the two-electron oxygen reduction reaction (2e^- ORR) to produce H_2O_2 from water and molecular oxygen. Despite recent progress, electrolyte effects of the electrochemical H_2O_2 production have remained little understood. We report a significant effect of alkali metal cations (AMCs) on the electrocatalytic H_2O_2 production on carbon catalysts in acidic



environments. The presence of AMCs at the electrified carbon interface shift the half wave potential of the 2e^- ORR from -0.48 V to $-0.22\text{ V}_{\text{RHE}}$. This cationic induced enhancement effect exhibits a uniquely sensitive on/off switching behaviour depending on the voltammetric protocol. Voltammetric and direct *in situ* X-ray photoemission spectroscopic evidence is presented that supports a controlling role of the potential of zero charge (PZC) of the catalytic enhancement. Depending whether the electrode potential is kept cathodic or even just briefly reaches values anodic of the PZC, AMCs accumulate at the electrified interface and enhance the 2e^- ORR or get repelled away from it, respectively. Density functional theory calculations associate the enhancement by the stabilization of the $^*\text{OOH}$ key intermediate. Based on this finding, we developed a refined reaction mechanism for the H_2O_2 production in presence of AMCs.

Hydrogen peroxide (H₂O₂) is a powerful green oxidizing agent and due to its use in various fields, such as in the pulp and paper bleaching industry¹, chemical synthesis^{2, 3}, and wastewater treatment^{4, 5} it is one of the cornerstones of the chemical industry. The global annual consumption of H₂O₂ reached a value of 4.4 billion USD in 2023 with a compound annual growth rate (CAGR) of 4.4 % in the forecast period of 2024-2032⁶. The ever-growing demand for H₂O₂ inspired research towards an alternative to the industrial anthraquinone process, which is currently producing 95% of the worldwide demand for H₂O₂. The process still suffers from high energy consumption, the generation of substantial amounts of organic by-products and risks associated with storage and extended transport routes of H₂O₂ stock solutions originating from the existence of only few centralized large scale anthraquinone process plants^{7, 8}. These obstacles could be overcome by the electrochemical two-electron oxygen reduction process (2e⁻ORR) for small-scale, on-site H₂O₂ production, where renewable energy sources can be applied as a power input:



Acidic hydrogen peroxide solutions are of great significance in the chemical industry because of their superior oxidizing ability when compared to alkaline solutions. Additionally, some reactions, e.g. the Electro-Fenton process for the wastewater treatment require acidic conditions in order to operate optimally (optimal performance within the pH range of 2.8-3.0⁹). Currently, only a limited number of expensive noble metal catalysts, such as platinum and palladium-based catalysts, have been identified as selective and stable for the 2e⁻ORR in acid media¹⁰⁻¹². Lower cost carbon-based catalysts have shown reasonable H₂O₂ selectivities at low pH values, but mainly at low current densities¹³⁻¹⁷. Reports at higher industrially relevant current densities do exist,¹⁸⁻²¹ yet tend to place focus on conventional cell performance indicators and fail to address the role of the microenvironment of the interface. Driven by the desire to overcome these shortcomings and to tap into our increasing atomic-scale knowledge regarding the complex electrolyte effects on the activity of catalysts for the electrochemical carbon dioxide reduction reaction (CO₂RR) and hydrogen evolution reaction (HER)²²⁻²⁵, scattered reports have appeared on pH effects^{26, 27} or electrolyte composition^{20, 28-31} on the 2e⁻ORR. However, a molecular understanding of alkali metal cations (AMCs) effects on the H₂O₂ electrosynthesis, especially in acidic media, is far from complete. Most reports ignore the key controlling role of the potential of zero charge (PZC) of the electrified interface. The PZC is the electrode potential at which the interface has no free surface charge. The net charge of the ions at the interface is determined by the applied potential relative to the PZC. At potentials cathodic of the PZC, the electrode is negatively charged and attracts cations, while at more anodic potentials than the PZC, the electrode attracts anions. The position of the PZC and the applied working potential window determine therefore the composition of the electric double layer.

The primary objective of this study is to explore and understand the impact of AMCs in the electrolyte on the kinetics and thermodynamics of the reaction pathway of the 2e⁻ORR towards H₂O₂ on carbon catalysts in strongly acidic conditions. Using experimental rotating ring disk surface voltammetry, time-resolved *in situ* X-ray photoemission spectroscopy (XPS) to track the accumulation of cations at electrified interfaces, and supporting density functional theory (DFT) calculations, we report, characterize, and unravel the mechanisms of the strong enhancement effect of AMCs on the 2e⁻ORR.

In order to investigate the influence of AMCs, in particular K^+ , on the kinetics of the $2e^-$ ORR towards H_2O_2 in 0.1 M H_2SO_4 , a Rotating Ring Disk Electrode (Pt ring, carbon disk RRDE) was employed. The smooth, polished glassy carbon (GC) disk was used as the catalyst material. As the PZC governs the surface charge of the electrode at any given applied potential, the experimental PZC of the GC disk was determined to have a value of around $+0.3 V_{RHE}$ in 0.1 M H_2SO_4 (**Figure S1**). The Pt- ring of the RRDE was held at constant $+1.2 V_{RHE}$. Due to a steady sulphate anion adsorption and poisoning (**Figure S2**), the Pt-ring current and the chemical H_2O_2 selectivity derived thereof can only be used as a qualitative probe for H_2O_2 formation³². Repeated cleaning of the Pt- ring by voltammetric pulses was not considered, since Pt dissolution and redeposition onto the GC had to be avoided³³. Importantly for this discussion, the $2e^-$ ORR voltammetric cycles were designed and performed with an upper turning potential (UTP) that was chosen either below or above the experimentally extracted PZC of the electrode.

Surface voltammetry in presence of AMCs below and above the PZC. **Figure 1 a)** shows the time dependent anodic RRDE voltammetric potential scans of the carbon electrode during the $2e^-$ ORR to H_2O_2 in 0.1 M H_2SO_4 + 0.05 M K_2SO_4 with an UTP below the PZC. The production rates of the H_2O_2 formation, as indicated by the ring current density, monotonically increased with increasing cycling number. The polarization curves stabilized after 190 cycles, when the characteristic $2e^-$ ORR voltammetric wave was fully apparent, which is coupled to the typical oxygen mass transport limiting range with a limiting current density of $\sim -3 \text{ mA cm}^{-2}$. The half wave potential of the 190th scan is $-0.22 V_{RHE}$ whereas for the first scan the potential for the same current density is $-0.48 V_{RHE}$. The corresponding Tafel slopes (**Figure S3 a)**) shift from -231 mV dec^{-1} for the first scan to -45 mV dec^{-1} for the 190th scan and reflect the increase in catalytic reactivity, likely associated with lower kinetic barriers along the ORR reaction pathways. We hypothesize that the emerging microenvironment at the reactive surface during voltage cycling beneficially affects binding energies of reactive intermediates of the $2e^-$ ORR. Examples of such intermediates are oxygenated surface species, such as oxygen $*O$ and peroxide intermediates $*OOH$ (where $*$ denotes an adsorption site)^{34, 35}. After cyclic voltammetry, SEM / EDX characterization of carbon surface revealed the formation of μm -sized K_2SO_4 crystals (**Figure S4**), consistent with salting out due to local accumulation of K^+ cations passing the solubility limit of K_2SO_4 ($111 \text{ g}\cdot\text{l}^{-1}$). Additionally, the voltammetric cycling exhibited a strong hysteresis behavior, with the anodic scan showing lower overpotentials for the $2e^-$ ORR than the cathodic scan (**Figure S5**). As corroborated further below, we attribute this to the fact that anodic scans originate at more negative electrode potential where AMCs had more time to accumulate near the reactive electrocatalytic interface. This hypothesis is supported by the effect of scan rate on the location and width of the hysteresis behavior (**Figure 1 b)**). Slow scans reveal a wide hysteresis with low catalytic reactivity on the cathodic, yet strong enhancement on the anodic scan. Counter to the expected voltammetric behavior of irreversible reactions, faster scans resulted in narrower hysteresis consistent with less time for cations to equilibrate their local distribution at very anodic or cathode electrode potentials. This observation points to the involvement of the K^+ cations in the electric double layer (EDL) and the charge dependent equilibrium. We safely exclude ACM intercalation and co-intercalation into the carbon surface as the prevalent origin of the gradual changes in the voltammetry, as these phenomena were reported at much more negative electrode potentials^{36, 37}. Also, on/off switching of cation effects (**Figure 1 d)**) with the UTP speaks against intercalation of cations in

the applied potential range. Finally, the influence of different K^+ concentrations was investigated (**Figure S5**). With increasing K^+ concentration the time to reach constant H_2O_2 reactivity decreased. All investigated concentrations of K^+ ($0.1\text{ M H}_2\text{SO}_4 + 0.1 / 0.05 / 0.01\text{ M K}_2\text{SO}_4$) ultimately resulted in a comparable $2e^-$ ORR activity enhancement. **Figure 1 c**) shows the analogous time-dependent anodic voltammetric scans during the $2e^-$ ORR in $0.1\text{ M H}_2\text{SO}_4 + 0.05\text{ M K}_2\text{SO}_4$ with an UTP above the PZC. The initial $2e^-$ ORR activity was identical to the initial activity with an UTP < PZC, but in contrast to **Figure 1 a**) no shift in the voltammetric wave, and hence electrocatalytic activity was observed over time (see Tafel analysis in **Figure S3 b**). The effect of the UTP is evidently striking. To better understand this phenomenon, the reversibility of the AMC induced activity enhancement was investigated (**Figure 1 d**). After initial 10 scans with an UTP < PZC, one single scan (11^{th}) was performed with UTP > PZC (green lines), followed by consecutive three scans with an UTP < PZC. The expected

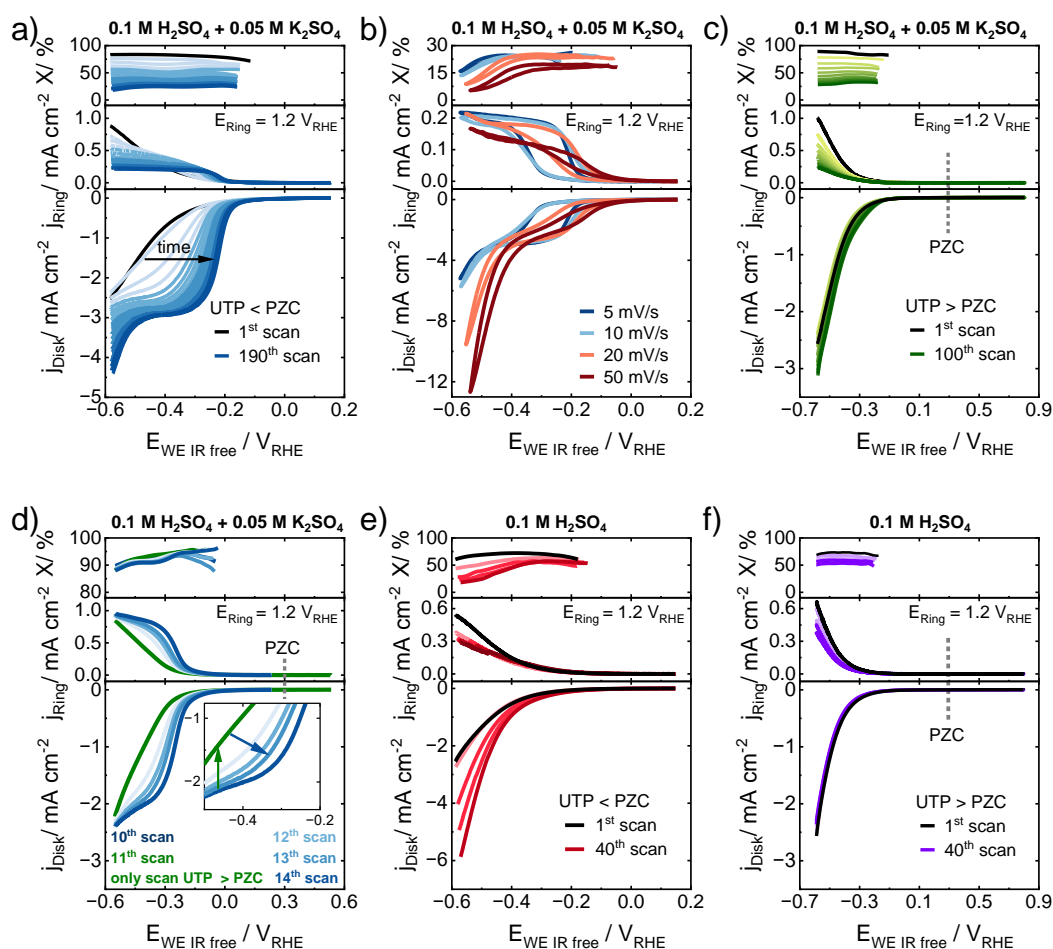


Figure 1 a-d) Effect of K^+ cations on the $2e^-$ ORR in $0.1\text{ M H}_2\text{SO}_4 + 0.05\text{ M K}_2\text{SO}_4$ on GC at 1600 rpm: a) Polarization curves for UTP below PZC. Time dependent activity improvement with first anodic scan (black) until constant activity after 190 scans (dark blue). Anodic scans with 5 mV/s in O_2 saturated electrolyte are shown. b) CVs at $5, 10, 20$ and 50 mV/s after 190 scans at 5 mV/s . c) Polarization curves UTP above PZC. Initial activity shown in black and 100^{th} scans shown in dark green. Anodic scans with 5 mV/s in O_2 saturated electrolyte are shown. d) Anodic scans with 10^{th} scan < PZC (dark blue), 11^{th} scan > PZC (green) and 12 - 14^{th} scan < PZC (light blue to blue), at 20 mV/s . Note: 1^{st} to 9^{th} scan below PZC are not shown. e) Polarization curves for UTP below PZC in $0.1\text{ M H}_2\text{SO}_4$, first scan shown in black and 40^{th} scan shown in dark red. f) Polarization curves for UTP above PZC in $0.1\text{ M H}_2\text{SO}_4$, initial first scan shown in black and 40^{th} scan shown in violet.

catalytic enhancement during the first 10 scans was followed by an abrupt immediate annulling/reset of the catalytic improvement on the 11th scan (UTP > PZC), followed by a continuously rising catalytic enhancement during scan 12 to 14, with UTP < PZC. This on/off experiment highlights the role of the working potential window relative to the PZC. To date, the 2e⁻ORR reactivity of carbon catalysts have been investigated at or above their PZC, which is why this cation surface accumulation effect has never been reported before utilizing RRDE techniques.

Surface voltammetry in absence of AMCs below and above the PZC. In contrast to the sharp AMC induced catalytic H₂O₂ production enhancement below the PZC, voltammetric cycling below the PZC in absence of AMCs in the electrolyte (pure 0.1 M H₂SO₄) led to no catalytic enhancement in the H₂O₂ production associated with an oxygen mass transport limited current density in the applied potential range. The Tafel slopes remained around 210 mV dec⁻¹ (**Figure S3 c**). Although the catalytic onset potentials remained constant over time, the disk current densities < -0.4 V_{RHE} gradually increased. Since the ring current densities did not reflect the rise in disk currents densities, we conclude a rise in the rate of the competing reactions under these conditions, such as the HER, the 4e⁻ORR to water, or the H₂O₂ reduction reaction. Efforts to use physicochemical SEM/ EDX maps of the carbon surface after voltammetry to get insight in the origin of the voltammetric behaviour remained inconclusive and are discussed in detail in the supporting information (**Figure S6**). Finally, **Figure 1 f** shows the anodic voltammetric scans for a UTP above the PZC in absence of AMCs in the electrolyte. Similar to **Figure 1 c**), no catalytic enhancement was evident over time. Here, the disk current densities remained almost constant over the entire potential range. Similar Tafel slopes of -209 and -221 mV dec⁻¹ were found for the first and 100th scans for a UTP above the PZC indicating an insignificant effect on the reaction kinetics (**Figure S3 d**). In order to investigate effect of AMCs on the HER, we performed voltammetric scans under Ar-saturated conditions with and without K⁺ cations in the electrolyte. In agreement with literature³⁸ a suppression of the HER due to the presence of K⁺ cations was confirmed (**Figure S7**). The suppression being stronger if a UTP below the PZC was applied. However, due to the low disk current densities under Ar-saturated conditions it can be concluded that the HER only plays a minor role within the applied potential windows.

In situ XPS in the K 2p core level range. To directly track the accumulation of AMCs at the reactive carbon interface, time-resolved *in situ* XPS measurements were carried out, utilizing a previously reported membrane-electrode flow cell³⁹. The goal of these measurements was the direct observation of the potential controlled accumulation and repulsion of K⁺ cations at and from the carbon electrode surface (tri-layer graphene on Nafion®117). Details of the carbon electrode fabrication and cell configuration are provided in the supporting information. Initially, the carbon electrode surface was divided into a given number of distinct spots of interest, which were measured in consistent order for each spectroscopic measurement. Survey spectra were taken before and after the electrochemical protocol (**Figure S8**). The applied potential protocol involved an applied electrode potential step and hold at +0.49 V_{RHE} for 4.5 h, followed by a potential step and hold at -0.61 V_{RHE} for 6 h, followed by a return to +0.49 V_{RHE} for 4 h. A number of spectra were taken during each potential step.

Figure 2 a) shows a selection of nine fitted high-resolution *in situ* XPS spectra of the carbon interface in the K 2p core-level region at the three applied electrode potentials (0.49, -0.61, 0.49 V_{RHE} from left to right) at three selected measurement times (time increase from bottom to top) for an identical spot. **Figure S9** shows the corresponding spectra in their full-width binding energy range, entailing the K 2p and C 1s core level regions. Spectral fitting required deconvolution of the K 2p_{3/2} (and to a lesser extent the K 2p_{1/2}) species and the C 1s species contribution with high core level shifts, as found in carbon atoms bonded to Nafion F atoms. **Figure 2 b)** shows the overlaid spectra for each time. **Figure 2 a) and b)** evidence that at +0.49 V_{RHE}, there is no accumulation of K⁺ cations near the carbon interface over 4.5 h. By contrast, at -0.61 V_{RHE}, the K 2p core level peaks gradually emerge in intensity with time, suggesting the accumulation of K⁺ cations at the interface. After returning to +0.49 V_{RHE}, the K 2p peak intensities decreased pointing to the slow migration of K⁺ cations away from the interface. Slight potential-dependent K 2p core level peak shifts can be attributed to charging effects, since the K⁺ cations are in no direct contact to the grounded carbon electrode. **Figure 2 c)** shows the mean total K 2p peak area ratio, averaged over all accessible spots of the sample, validating that the molar concentration of K⁺ cations is controlled by the applied electrode potential. The averaged K 2p peak area ratio for each spot of the sample is detailed in **Figure S10**. To exclude an accidental onset of K⁺ cations accumulation after 4.5 h at 0.49 V_{RHE} and to

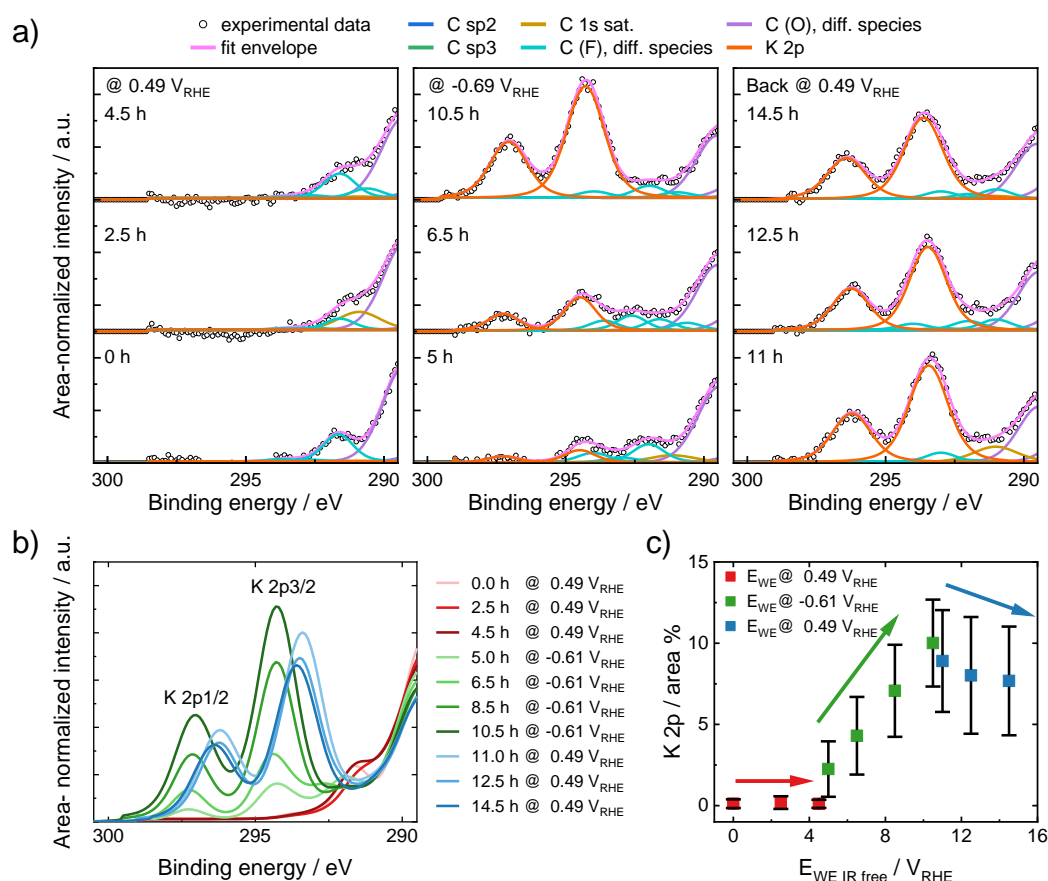


Figure 2 a) Exemplary fitted XPS high-resolution spectra of one spot of tri-layer graphene on Nafion®117 in the K 2p region over time at different potentials. Spectra were acquired at a pass energy of 20 eV and a source energy of 1000 keV. **b)** Stacked area-normalized intensities for K 2p peak for same spot as in a) over time. **c)** Averaged K 2p peak area percentage of all measured spots over time as function of applied potential.

validate that the K^+ cation accumulation can be triggered solely by shifting the electrode potential, an additional experiment with a shorter 30 min initial potential hold at 0.49 V_{RHE} was conducted (**Figure S11**). The K 2p core level peaks increased as soon as -0.61 V_{RHE} was applied, proving that the accumulation K^+ cations at the cathode is mainly influenced by the applied potential and not by the hold time. The surprisingly slow time scale of the K^+ cations accumulation and repulsion is attributed to the fact that K^+ cations have to cross the entire Nafion membrane before they will enter the membrane-carbon interface. Also, as the carbon catalyst faces the vacuum region, this may lead to a relatively dry membrane-catalyst interface which might slow down solvent assistant ion migration. Conversely, once the K^+ cations have passed the membrane entering the carbon electrode interface they may get trapped there during interfacial charge reversal.

Density functional theory (DFT) calculations. To substantiate and explain the experimental findings, DFT calculations were carried out with the Quantum ESPRESSO⁴⁰ simulation package, utilizing GGA-PBE functionals to describe the exchange-correlation energy⁴¹ and SSSP pseudopotentials to account for the core electrons⁴². For more computational details the reader is referred to computation details section in the supporting information. Previous work investigating the cation effect on different reactions by a variety of different approaches. For instance, Zhang *et al.* also found that alkali metal cations in acidic electrolytes can improve the H_2O_2 electrogeneration significantly utilizing an electrolyser unit²⁰. In their work, *ab-initio* molecular dynamics (AIMD) calculations were employed to show that Na^+ cations adsorb on the electrode surface and create a local coordination environment that drives H^+ atoms away from the *OOH intermediate, thus promoting the stabilization of the H_2O_2 molecule. However, the authors noted, that it is not possible to observe the same cation effect applying the RRDE technique due to the strong agitation and the low steady-state surface concentration of alkali metal cations at the electrode surface. Resasco *et al.* on the other hand, investigated this effect for the CO_2RR , and employed constrained minima hopping calculations to determine the solvation shell of different AMCs⁴³. Na^+ and K^+ cations, for instance, accommodate 5-6 water molecules on their solvation shells. The authors noted that larger solvated cations are more energetically favoured at the outer Helmholtz plane which results in a higher cation coverage for these species, thus increasing the local field strength on the adsorbates⁴³. Herein, we delve into the local field effect that these cations have on the $2e^-ORR$ thermodynamics, modelling it through an explicitly applied field⁴³⁻⁴⁵. The theoretical calculations show the stabilization of the ORR intermediates, in terms of Gibbs free energy difference, when the local field effect is considered, as can be seen in **Figure 3**. The effect is similar among the different carbon functionalizations (investigated carbon functionalizations can be found in **Figure S12**), with a decrease in ΔG for all reaction intermediates following the increase in the local field^{44, 45}. The *OOH intermediate is widely considered to be the key intermediate of the $2e^-ORR$ and can be therefore used as an activity descriptor^{34, 35}. Overall, the distance between the *OOH intermediate and the catalytic surface stays the same. However, under a positive field, the hydrogen atom turns towards the solution and away from the surface. This geometry change might also contribute to the additional energy gain observed in the ΔG^{*OOH} values. When the applied field is positive ($E > 0 V$), ΔG^{*OOH} decreases 0.2 - 0.8 eV, and this accounts for the observed decrease in the onset potential (**Figure 1 a**).

Figure 4 shows the activity volcano plot for the 2e⁻ORR. Without any applied field, the selected defects and functional groups lie on the weak *OOH binding region of the volcano plot⁴⁶. The additional stabilization observed when an applied field is considered (in this case, E = 0.6 V) results in a shift toward the top of the volcano in three of the considered structures 555-777, 55-77, and Vac-O, which is in agreement with the experimental observations and with the literature⁴³⁻⁴⁵. This shift is enough to account, from a qualitative perspective, for the changes observed in the half wave potential, from -0.48 V to -0.22 V_{RHE} when K⁺ cations are added to the electrolyte. Considering these results, we propose a new reaction mechanism by which the key reaction intermediate, the *OOH intermediate, is stabilized by the positive local field induced by AMCs, such as K⁺, acting as Lewis acids (Equation 2 and 3):

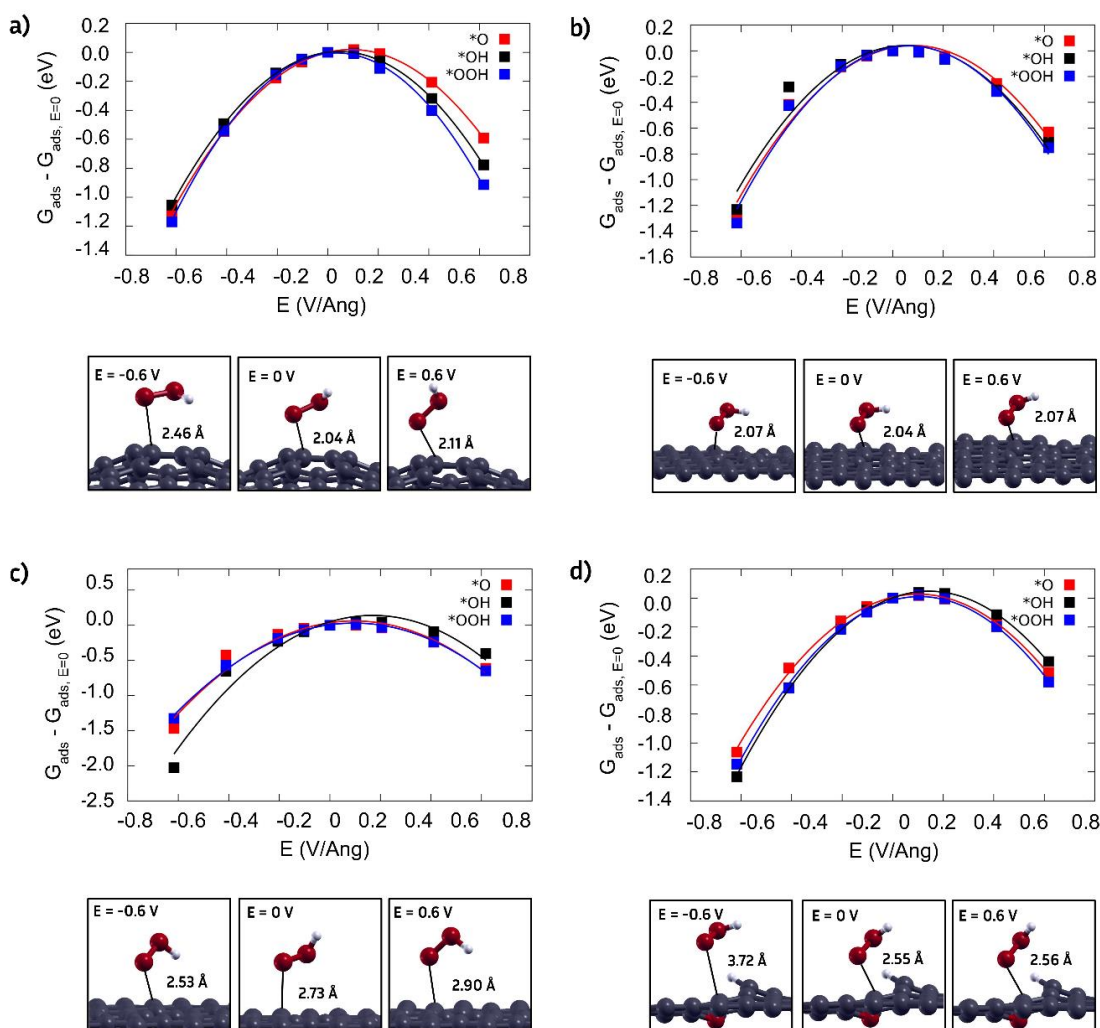
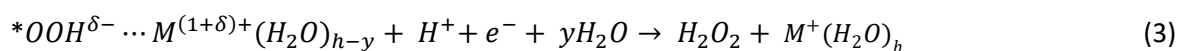
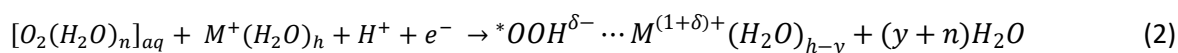


Figure 3 Field effect on ORR adsorbates and the relaxed conformation of the *OOH intermediate for different carbon defects and functional groups: 555-6-777 (a), 555-777 (b), 55-77 (c), and vac-O, carbon vacancy substituted by oxygen and hydrogen (d).

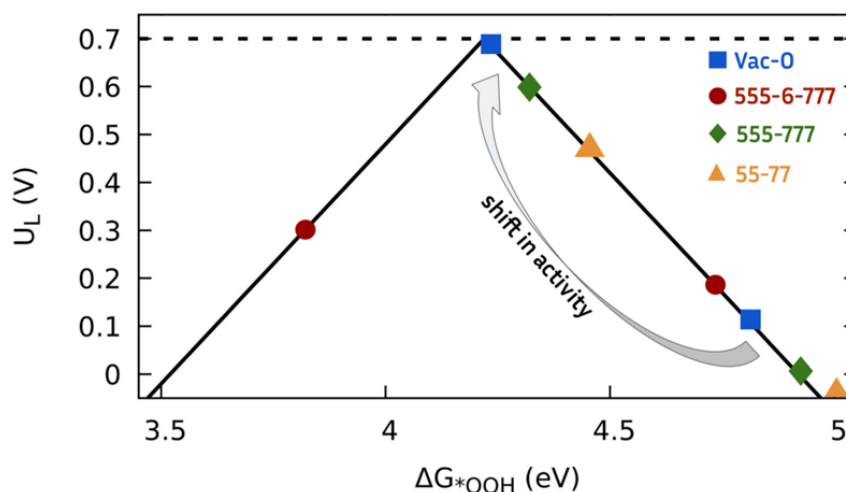


Figure 4 Volcano plot for the O_2 electroreduction to H_2O_2 with the limiting potential (U_L) as a function of ΔG^*_{OOH} . The equilibrium potential for this reaction (0.695 V vs SHE) is indicated by a dashed line. The shift in activity arrow indicates the new ΔG^*_{OOH} and U_L values when the applied field changes from $E = 0$ V to $E = 0.6$ V.

In conclusion, this contribution has combined theory and experiments to explore the significant cation-induced electrocatalytic enhancement effects on the $2e^-$ ORR towards H_2O_2 in acidic solutions, by focusing on K^+ cations as an example. We showed and explored the cation-induced enhancements in a three-electrode liquid electrode RRDE environment, where the catalytic enhancement during voltammetric cycling showed a strong dependence on the UTP relative to the PZC. Due to the enhancement effect a H_2O_2 -selective voltammetric wave with mass transport limited current consistent with a $2e^-$ transfer process emerged. The half wave potential was shifted anodically from $-0.48 V_{\text{RHE}}$ to $-0.22 V_{\text{RHE}}$. Time-resolved *in situ* XPS measurements visualized the potential-dependent enrichment and repulsion of K^+ cations from the working electrode surface. Finally, we were able to explain the experimentally observed cation effects using DFT calculations, whereby we were able to formulate a new reaction mechanism for the $2e^-$ ORR by the cation induced stabilization of the key reaction intermediate, the $^*\text{OOH}$ intermediate. The presented insights into the significant influence of the electrolyte on the electrocatalytic $2e^-$ ORR in acidic conditions pave the way for a communalisation of the process utilizing cheap carbon catalysts and could also trigger future work on other promising $2e^-$ ORR catalyst systems.

Declaration of interests

The authors declare no competing financial interest.

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Associated Content

The Supporting Information is available free of charge at XXX

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