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Enhancing oxygen reduction electrocatalysis by tuning interfacial hydrogen bonds

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Proton activity at the electrified interface is central to the kinetics of proton-coupled electron transfer (PCET) reactions for making chemicals and fuels. Here we employ a library of protic ionic liquids in an interfacial layer on platinum and gold to alter local proton activity, where the intrinsic oxygen-reduction reaction (ORR) activity is enhanced up to fivefold, exhibiting a volcano-shaped dependence on the pK_a of the ionic liquid. The enhanced ORR activity is attributed to strengthened hydrogen bonds between ORR products and ionic liquids with comparable pK_a s, resulting in favourable PCET kinetics. This proposed mechanism is supported by in situ surface-enhanced Fourier-transform infrared spectroscopy and our simulation of PCET kinetics based on computed proton vibrational wavefunctions at the hydrogen-bonding interface. These findings highlight opportunities for using non-covalent interactions between hydrogen-bonded structures and solvation environments at the electrified interface to tune the kinetics of ORR and beyond.

nderstanding proton-coupled electron transfer (PCET) processes is critical to controlling the reaction kinetics in biochemistry¹, organic chemistry^{1,2}, inorganic chemistry^{3,4}, environmental chemistry⁵ and electrochemistry^{2,6}. In particular, PCET steps have been investigated extensively in recent research on catalysts for making energy carriers or solar fuels^{2,7} including water splitting^{2,7}, and for converting energy carriers in fuel cells to generate electricity^{4,6} including the oxygen-reduction reaction (ORR)⁶. It is currently believed that the ORR mechanism⁶ involves PCET steps on surface metal sites, which can involve one key intermediate on metals such as gold⁸ for the two-electron ORR $(O_2 + 2H^+ + 2e^- \rightarrow H_2O_2)$ $0.68 V_{RHF}$, where V_{RHF} is the voltage relative to the reversible hydrogen electrode), that is, *OOH (refs. 8,9), and three key intermediates on metals such as platinum^{10,11}, that is, *OOH, *O and *OH, for the four-electron ORR $(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O, 1.23V_{RHE})$. Conventional design of catalysts involves tuning the surface electronic structure and covalent interactions with reaction intermediates (surface binding or adsorption strength), which has led to notable advances in the intrinsic activity of the ORR by tuning the strain¹², the ligand effect¹³ and the surface orientation¹⁴. For example, Pt₃Ni(111) (ref. ¹⁵) has been shown to exhibit intrinsic ORR activity tenfold greater than that of Pt(111) at $0.9V_{RHE}$, and polycrystalline PtGd16 exhibits fivefold enhancement compared to polycrystalline Pt.

Recent studies have shown that changing electrolyte compositions can notably alter the kinetics of electrochemical reactions such as the ORR¹⁷⁻²¹ and the hydrogen-oxidation reaction²², highlighting new opportunities in non-covalent interactions from using the chemical physics of electrolytes to control activity. While the pH of the electrolyte, which represents proton activity, does not greatly alter the ORR activity of metals such as platinum²³, increasing pH can notably increase the ORR activity on weakly interacting metals such as gold^{18,19}, where the activity in bases is much higher than that in acids. Moreover, modifying platinum-based catalysts with protic ionic liquids^{17,20,21} is shown to enhance the ORR activity in acid, where ionic-liquid-modified PtNi nanoparticles have approximately threefold greater intrinsic ORR activity than pristine PtNi (ref. 17), and ~20-fold greater activity than commercial Pt/C (ref. 20). Although this increase in the ORR activity has been attributed to the increase in hydrophobicity at the interface between platinum and ionic liquids²¹ and oxygen solubility in ionic liquids^{17,24}, it is not apparent how to design new catalysts to control the catalytic activity of the ORR and other reactions using this strategy. Considering the ionic liquids used in previous studies^{17,20,21} have different pK_a from the acidic electrolyte and the $\Delta p K_a$ values between cations and anions were found to be correlated with the open-circuit potential of H_2/O_2 fuel cells^{25,26}, it is postulated that the interfacial proton activity of ionic liquids can alter the proton transfer or PCET kinetics on metals such as platinum and gold, and thus the ORR activity, which is the focus of this work.

In this article we employ a library of protic ionic liquids in an interfacial layer to tune the ORR kinetics of platinum and gold in acid. We hypothesize that the protic cations in the ionic liquids can serve as intermolecular proton relays between the protons in the bulk electrolyte and near the metal surface, where altering the proton activity (or pK_a) using different protic cations provides opportunities to examine how local proton activity near the active sites can influence the ORR kinetics. A library of protic cations with different pK_a values was used ($[C_4C_1im]^+$ pK_a=23.3 (ref. ²⁷), [TMPim]^+ $pK_a = 21.3$ (ref. ²⁷), [MTBD]⁺ $pK_a = 15.0$ (ref. ²⁸), [DBU]⁺ $pK_a = 13.5$ (ref. ²⁸), [DEMA]⁺ $pK_a = 10.3$ (ref. ²⁹), [TEMEDA]⁺ $pK_a = 8.9$ (ref. ³⁰), $[C_4 Him]^+ pK_a = 7.1$ (ref. ³¹); see Methods for abbreviations) to influence the ORR activity of gold and platinum, which catalyse the ORR via the 2e⁻ (ref. ¹⁸) and 4e⁻ (ref. ³²) pathways, respectively, in acid. The ORR activity of gold and platinum was found to increase with the presence of protic cations, where the maximum enhancement

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Fig. 1 Tuning local proton activity for the ORR. The local proton activity is altered for the ORR catalysed on the surface of metallic catalysts by adding a thin layer of protic ionic liquids, where the pK_a value can range from 7.1 to 23.3 (refs. ^{27–31}). The anion of all the ionic liquids used in this work was bis(trifluoromethanesulfonyl)imide (NTf₂).

was obtained when the pK_a values of the protic cations and the reaction intermediate in the ORR rate-limiting step are similar. The ORR activity enhancement can be attributed to the stronger hydrogen bond between protic cations and the rate-limiting ORR intermediate, which is supported by in situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS). Further support came from predicted PCET kinetics based on computed proton vibrational wavefunctions at the hydrogen-bonding interface, where the stronger hydrogen bond between protic cations and ORR intermediates led to faster proton tunnelling kinetics, giving rise to greater ORR exchange current density. Our work reveals the role of local pK_a and interfacial hydrogen-bond strength on the kinetics of PCET and electrochemical reactions, which highlight new opportunities to further enhance electrocatalytic activity of the O2 CO2 and N2 reduction reactions, and beyond, by tuning local proton activity near the active sites.

Results

pK_a-dependent ORR activity of catalysts with ionic liquids. A thin layer of ionic liquids was added to the surface of Au/C and Pt/C to tune the local proton activity for the ORR, where the pK_a of protic cations could be altered (Fig. 1). The ORR activity of Au/C (6.0 nm Au) and Pt/C (19 wt% 1.7 nm Pt) with and without protic cations was measured using rotating disk electrode measurements as shown in Fig. 2a,b, respectively. The ionic liquid layer thickness with protic cations on the surface of Au/C and Pt/C was estimated to ~1 nm (see Supplementary Fig. 1 for details). The catalysts with protic cations

showed enhanced activity compared to those without protic cations, as indicated by the positive shifts in the half-wave potential in the voltammetry data. The ORR kinetic currents were extracted from the data in Fig. 2a,b and Supplementary Fig. 2 using Koutecky-Levich analysis, from which the specific and mass activity were obtained by normalizing the kinetic ORR current (Supplementary Fig. 3) by the electrochemically surface area from cyclic voltammetry measurements (Supplementary Figs. 4 and 5) and metal mass (Supplementary Fig. 6), respectively. The specific ORR activity for Au/C at $0.4 V_{RHE}$ can be enhanced up to approximately fivefold with protic cations relative to pristine Au/C as shown in this work, while that of Pt/C at 0.9 V_{RHE} can be increased approximately threefold compared to pristine Pt/C (19 wt%, ~ 190 $\mu A \text{ cm}_{Pt}^{-2}$) as shown in this work and previous studies^{21,33}. Similar activity trends and enhancement were found for polycrystalline gold (approximately fourfold at 0.3 V_{RHE}, Supplementary Fig. 7a) and platinum (approximately twofold at 0.9 V_{RHE}, Supplementary Fig. 7b). The exchange current density of the ORR was extracted for Au/C ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$, 0.68 V_{RHE}) and for Pt/C (O₂+4H⁺+4e⁻ \rightarrow 2H₂O, 1.23 V_{RHE}) using the Butler-Volmer theory in Supplementary Figs. 8 and 9, respectively. These observations suggest that the local proton activity at the metal/electrolyte interface can considerably influence the ORR kinetics.

The ORR activity of both Au/C and Pt/C was found first to increase and then decrease, exhibiting a volcano trend, as a function of the pK_a of the protic cations, as shown in Fig. 2c,d, respectively. The maximum ORR activity enhancement for Au/C was found for



Fig. 2 | pK_a -dependent ORR activity. The ORR activity on ionic-liquid-modified Au/C and Pt/C measured in O₂-saturated 0.1 M HClO₄, with a scan rate of 10 mV s⁻¹ and a rotation speed of 1,600 r.p.m. **a,b**, Background and iR- corrected ORR polarization curves of ionic-liquid-modified Au/C (**a**) and Pt/C (**b**). **c,d**, The relationship between the enhancement of the ORR specific kinetic currents on ionic-liquid-modified Au/C (**c**) and Pt/C (**d**) as a function of the pK_a of protic cations in ionic liquids. Error bars represent standard deviations of at least three independent measurements. The loading of platinum was controlled at 20 µg cm⁻² and the loading of gold was controlled at 40 µg cm⁻²; 0.05 wt% Nafion was added to the catalytic layer.

 $[DEMA][NTf_2]$ with a pK_a of 10.3, which is similar to the ORR product on gold, H_2O_2 , with a pK_a of 11.6. The production of H_2O_2 on Au/C and ionic-liquid-modified Au/C was measured with a rotating ring-disk electrode (Supplementary Fig. 10), which revealed that the number of electron transfers for the ORR was 2.0-2.2. This result confirms that H₂O₂ is the main product for ionic-liquid-modified Au/C as well as for pristine Au/C. In acid, the first PCET step of the ORR on gold $(O_2 + H_3O^+ + e^- \rightarrow OOH_{Au} + H_2O)$ has similar kinetics to the second step (OOH_{Au} + H₃O⁺ + $e^- \rightarrow$ H₂O₂ + H₂O), as indicated by the 0.09 eV difference in the activation barrier from density-functional theory (DFT)³⁴. As increasing pH is shown to promote the rate of the first step by several orders of magnitude¹⁹, the second step becomes rate limiting for the overall kinetics with increasing local pH. Therefore, we propose that the ORR kinetics on gold with interfacial ionic liquids is limited by the PCET kinetics of OOH_{Au} to form H_2O_2 (OOH_{Au} + N-H⁺ + $e^- \rightarrow H_2O_2 + N$)⁸ (detailed kinetic analysis is shown in Supplementary Fig. 11). This hypothesis is in agreement with previous kinetic measurements of the ORR in organic solvents, where the first electron transfer step $(O_2 + e^- \rightarrow O_2^-)^{35}$ is more than 10³ times faster than the second PCET step $(O_2^- + e^- + H_2O \rightarrow OOH^- + OH^-)^{36}$. Further support comes

from the observation that OOH_{Au} has been detected as the stable ORR intermediate accumulating on gold by in situ ATR-SEIRAS⁹ and in situ surface-enhanced Raman spectroscopy³⁷. Therefore, it is proposed that the different pK_as altered the kinetics of the second PCET step for ORR on gold in ionic liquid (OOH_{Au}+N-H⁺+ $e^- \rightarrow H_2O_2 + N$) and consequently tuned the overall ORR kinetics. This hypothesis departs from the decoupled proton–electron transfer mechanism outlined by Koper¹⁹, where increasing kinetics with increasing pH for one-electron reduction can be attributed to enhanced electron-transfer kinetics on the RHE scale.

The maximum ORR activity enhancement for Pt/C occurred for [MTBD][NTf₂] with a pK_a of 15.0, which is similar to the ORR product in the rate-limiting step, H₂O, with a pK_a of 15.7. Previous DFT studies have shown that the PCET of adsorbed OH on platinum to form H₂O is rate limiting (OH_{Pt}+H⁺+ e^- →Pt+H₂O)⁸, which is supported by ambient pressure X-ray photoelectron spectroscopy¹⁰ and in situ electrochemical surface-enhanced Raman spectroscopy^{11,38}. The coverage of intermediates (O_{Pt} and OH_{Pt} on platinum) is about 20–30% at ORR-relevant potentials^{10,38} and that of cations was estimated to be 17–30% on platinum (Supplementary Table 1). Thus, the coverage of cations is comparable to the coverage of ORR

intermediates, enabling each adsorbed ORR intermediate on the surface to potentially take a proton from the ionic liquid during the ORR. Therefore, these results show that the kinetics of ORR on gold and platinum could be regulated by the pK_a of protic cations at the interface; these cations can work as proton donors near the active sites, catalysing the rate-limiting PCET. The maximum ORR activity is obtained with the minimum pK_a difference between the protic ionic liquid (proton donor) and the rate-limiting ORR product (proton acceptor). This observation is further supported by the measurement on Au/C in 0.1 M NaClO₄ and Ag/C in 0.1 M HClO₄, in which the number of electron transfers for the ORR is close to 3, and both H₂O₂ and H₂O are ORR products (Supplementary Fig. 12c,d and Supplementary Note 1). The maximum ORR activity enhancement was found for $[DBU][NTf_2]$ with a pK_a of 13.5 (Supplementary Fig. 12e,f and Supplementary Note 1), which is between the pK_a of H₂O and H₂O₂. Therefore, the results further support our opinion that the pK_a of the cation can affect the ORR kinetics and is correlated with the intermediates of the ORR pathway.

Because the thermodynamic driving force of PCET reactions diminishes as the pK_a difference between the proton donor and acceptor reduces, and the reorganization energy (λ) fitted by the Marcus–Hush–Chidsey (MHC) theory is similar for different ionic liquids (Supplementary Fig. 13), we propose that the enhancement in the ORR activity with different ionic liquids can be attributed to the difference in the interfacial hydrogen-bond structure as predicted previously by the PCET theory for homogeneous reactions^{3,4}, which will be examined below by in situ ATR-SEIRAS experiments and computation.

pKa-dependent interfacial hydrogen-bond structure. In situ ATR-SEIRAS was performed on gold and platinum thin films chemically deposited on a silicon prism; this technique detected ORR intermediates and revealed the interactions between protic cations in ionic liquids and ORR intermediates by monitoring the stretching frequency of hydrogen-bonded species of protic cations as influenced by the formation of ORR intermediates and product as a function of potential. Potential-dependent in situ ATR-SEIRA spectra were collected from [MTBD][NTf₂]-modified gold thin-film surface (estimated to have a thickness of ~50 nm for gold and ~20 µm for [MTBD][NTf₂]). Difference spectra subtracted from that collected at open-circuit voltage are shown in Fig. 3, along with that of bulk [MTBD][NTf₂] and [MTBD][NTf₂] with water (0.5 M water). Two sharp peaks at 1,632 and 1,603 cm^{-1} (Fig. 3a), resulting from the stretching mode of C=N-H⁺ and C=N in the cation³⁹, respectively, grew with decreasing potential. The increased peak intensities can be attributed to having more protic cations on the gold surface with decreasing potential, which is in agreement with increasing peak intensities of C-N stretching⁴⁰ from protic cations at 1,231 cm⁻¹ (Fig. 3b). Similar peaks to those observed on gold were found on [MTBD][NTf₂]-modified platinum thin-film surface (Supplementary Fig. 14), which also grew with decreasing potential.

Two new peaks, at 1,263 and 3,238 cm⁻¹, emerged (Fig. 3b,c) with decreasing potential, which can be assigned to the bending (H–O–O) of HOO adsorbed on gold⁹ and the stretching of N–H⁺···OOH_{Au} of [MTBD][NTf₂], respectively. The assignment of the broad feature at 3,238 cm⁻¹ is supported by DFT calculations, where the computed N–H⁺···OOH_{Au} stretching of [MTBD][NTf₂] was determined to be 3,267 cm⁻¹ (Supplementary Table 2), in good agreement with the experimental observation. This new broad peak at ~3,238 cm⁻¹ is red-shifted compared to the N–H⁺ stretching of bulk [MTBD] [NTf₂] with and without water added (~3,400 cm⁻¹ in Fig. 3c), indicating the presence of hydrogen-bond interactions between protic cation and ORR intermediates such as [MTBD]N–H⁺···OOH_{Au}. These two peaks at 1,263 and 3,238 cm⁻¹ grew at the expense of the peak at 3,583 cm⁻¹, attributable to the O–H stretching⁴¹ of water dissolved in the [MTBD][NTf₂] in Fig. 3c and Supplementary Fig. 14,

which indicated reduction of water adsorbed on the surface with decreasing potential.

Changing the pK_a of the protic cations was found to red-shift the N-H+...OOH_{Au} stretching at ORR-relevant potentials (Fig. 4 and Supplementary Figs. 15 and 16). The N-H+...OOH_{Au} stretching frequency decreased from 3,429 cm⁻¹ for [C₄Him][NTf₂] with a pK_a of 7.1 in Fig. 4c, to $3,238 \text{ cm}^{-1}$ for [MTBD][NTf₂] with a pK_a of 15.0 in Fig. 4a, to \sim 3,000 cm⁻¹ for [DEMA][NTf₂] with a pK_a of 10.3 in Fig. 4b, at $0.2 V_{RHE}$. These assignments are supported by DFT calculations (Supplementary Table 2), which also show the two fine peak features at ~3,000 cm⁻¹ for [DEMA][NTf₂] with the maximum ORR activity, with the feature at 2,985 cm⁻¹ due to the stretching of [DEMA]N-H+...OOH_{Au} and the feature at 3,024 cm⁻¹ due to [DEMA]N-H+...OHOH. Further support for these assignments came from the observed peak growth as expected for increasing ORR intermediates with decreasing potential (Supplementary Figs. 15-17). Weakening the N-H+ (proton donor) stretching of N-H+...OOH_{Au} from [C₄Him][NTf₂] to [DEMA][NTf₂] indicates stronger hydrogen-bond interactions in N-H+...OOH_{Au} as shown from previous infrared spectroscopy studies of hydrogen-bonded species⁴², suggesting the strongest hydrogen-bond is found for $[DEMA][NTf_2]$ with a similar pK_a (10.3) to that of H_2O_2 (11.6). This observation is in agreement with general trends that the hydrogen bond would become stronger when the difference between the pK_a value of proton donor and acceptor decreases as shown from thousands of hydrogen-bond structures from the Cambridge Structural Database including N-H+...O, N-H+...N, and so on⁴³. Therefore, the maximum ORR activity found on gold in the presence of [DEMA][NTf₂] is associated with the strongest hydrogen-bond interaction between N-H+...OOH (Fig. 4g). Considering the rate of the ORR on gold is limited by the PCET from OOH_{Au} to form H_2O_2 on gold in ionic liquids (OOH_{Au} + N-H⁺ + $e^- \rightarrow$ H₂O₂ + N), strengthening the H…OOH facilitated by protic cations with comparable pK_a such as [DEMA]N-H⁺ would enhance ORR kinetics.

Similar to gold, the maximum ORR activity found on platinum in the presence of [MTBD][NTf₂] is associated with the strongest hydrogen-bonding interaction between N-H⁺ and OH of species such as N-H+...OH_{Pt} among the protic cations examined in this study, as shown in Fig. 4d-f,h and Supplementary Figs 18-20. This assignment is in agreement with the detection of Pt-OH as the dominant ORR intermediate by in situ surface-enhanced Raman scattering and X-ray photoelectron spectroscopy^{10,11,38} and previous DFT findings that the PCET of OH adsorbed on platinum is rate limiting for the ORR⁸. Further support came from the agreement between the experimentally observed and DFT-calculated (Supplementary Table 2) wavenumbers for N-H⁺ stretching, where the computed values for [MTBD]N-H+...OH_{Pt}, [DEMA]N-H+...OH_{Pt} and [C₄Him] $N-H^+\cdots OH_{p_t}$ were found to be 3,089, 3,188 and 3,335 cm⁻¹, respectively. Like gold, the N⁺-H stretching for the protic cation with the maximum ORR activity has one additional feature to [MTBD] N-H⁺···OH_{Pt} at 3,089 cm⁻¹, which can be attributed to [MTBD]N- $H^+\cdots OH_2$ at 3,215 cm⁻¹ as supported by DFT (Supplementary Table 2), revealing the presence of the ORR intermediate (OH_{Pt}) and final product (H₂O) in the rate-limiting step. Considering the PCET from OH_{Pt} to form H_2O ($OH_{Pt}+N-H^++e^- \rightarrow H_2O+N$) is rate limiting, strengthening H…OH facilitated by protic cations with comparable pK_a such as [MTBD]N⁺-H would enhance the ORR kinetics. In addition, we measured the water solubility of different ionic liquids to discuss the potential effect of water in ionic liquid; the results are shown in Supplementary Table 3. We found there was no apparent correlation between bulk water content in ionic liquids and ORR activity. Considering the water content at the interface, we further examined the water signal at the electrode interface by in situ ATR-SEIRAS. When the ORR current density increased with decreasing potential, the infrared intensity of OH stretching (3,600-3,300 cm⁻¹) and H-O-H bending (1,600-1,700 cm⁻¹) of water decreased and the

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Fig. 3 | Potential-dependent infrared spectra of [MTBD][NTf₂]-modified gold. In situ ATR-SEIRAS measurement on a [MTBD][NTf₂]-modified gold electrode in oxygen-saturated 0.1 M HClO₄: C=N stretching region (**a**), O-O-H bending region (**b**) and X-H (X = N, O) stretching region (**c**). Spectra were obtained during potential steps swept from 0.2 to $0.6 V_{RHE}$ in 0.1 M HClO₄. The blue curves show the infrared spectrum of pristine [MTBD][NTf₂] and the purple curve shows the infrared spectrum of pristine [MTBD][NTf₂] with 0.5 M water. The cumulative number of 256 was used at a 4 cm⁻¹ resolution. Spectra were subtracted with respect to a reference spectrum obtained at open-circuit voltage in 0.1 M HClO₄.

cation signal increased (Supplementary Figs. 14–16 and 18–21). This phenomenon indicated that cations could increasingly adsorb on the metal surface and remove water with decreasing potential during the ORR. This finding agrees with previous work on the interface between gold and humid ionic liquids, where cations of ionic liquid are shown to accumulate on the gold surface at ORR-relevant potentials⁴⁴, and there is no adsorption of water at the gold surface in the potential window of -0.4 to 0.4 V⁴⁵. Therefore, based on our ATR results and previous work^{44,45}, water adsorption in ionic liquid at ORR-relevant potentials is insignificant, and the variation of ORR activity of different ionic liquids is mainly dependent on the change of hydrogen-bonding structure between cations and ORR intermediates.

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pK_a-dependent PCET kinetics in the ORR. To further explore the physical origin of ORR activity enhancement by modification of ionic liquids, we fitted the ORR polarization curves of pristine gold and ionic-liquid-modified gold by the MHC theory. The results show that λ is 1.59 eV in 0.1 M HClO₄ (Supplementary Fig. 13a) and ~1 eV in ionic liquids (Supplementary Fig. 13b–d). λ can be correlated with the dielectric constant of local reaction environments⁴⁶. By fitting λ using the Born model, we found the dielectric constants in the local reaction environment of ionic-liquid-modified gold to be $\sim 2.5-2.6$, which is clearly lower than that of water on gold (~ 3.6) under the ORR. Further details are available in Supplementary Note 2. The decrease in the dielectric constant can be related to the hydrophobic environment created by ionic liquids47, which consequently reduced λ and enhanced the ORR activity. Therefore, the hydrophobicity of the surface could benefit the activity of the ORR, in agreement with previous work^{21,24}. The variation of pK_a and hydrogen-bonding structure mainly alter the exchange current density (Supplementary Fig. 13b–d). Since the λ of ionic liquids fitted by MHC is in the range from 1.03 to 1.05 eV, and this difference is insignificant due to experimental uncertainties, the changes in the exchange current density are dominated by the increasing pre-exponential factor (Supplementary Table 4), which has been correlated to the hydrogen-bonding structure^{3,4}. On the other hand, the ORR of gold in 0.1 M HClO4 exhibits a higher pre-exponential factor than in ionic liquids; although the exchange current density is low because of the high λ , an increasing pre-exponential factor may result from favoured proton transfer via the hydrogen-bonding network in water. However, the interfacial water forms different types of hydrogen-bond networks and it is challenging to identify specific structures of hydrogen bonds for delivering protons to intermediates, which requires further study in the future. Moreover, it should be noted that the modification of ionic liquids would also tune the coverage of *O and *OH on the surface, which has been proposed to be one of the sources of the enhancement of ORR kinetics via ionic-liquid modification^{21,24}. However, this effect would not change the correlations observed on the ionic-liquid-modified catalysts here because all the ionic liquids tested would be expected to have similar effects on the coverage of *O and *OH. Therefore, to reveal the hydrogen-bonding effect on exchange current density and pre-exponential factor, the discussion below will focus on the effect of the interfacial hydrogen-bonding structure between ionic liquids and intermediates and their correlation with PCET kinetics.

Here we compute the exchange current densities of PCET kinetics (Fig. 5a) from select protic cations in the rate-limiting ORR step on gold (N-H⁺...OOH_{Au} + $e^- \rightarrow$ H₂O₂ + N) and platinum (N- $H^+\cdots OH_{Pt} + e^- \rightarrow H_2O + N$ using reported methods^{3,4}. While the minimum point of proton potential is close to the proton donor side (for example, the N atom of N-H+...OOH_{Au}) before electron transfer, the reaction intermediate (such as adsorbed OOH or OH) accepts one electron from the electrode and lowers the proton potential, enabling proton transfer to form the product, where proton and electron transfer occurs simultaneously³. The transferring proton was treated by quantum mechanics and the proton vibronic states were computed from the proton potentials of [MTBD]N-H+...OOH_{Au} (Supplementary Fig. 22a), [DEMA]N-H+...OOH_{Au} (Supplementary Fig. 22b), [C4Him]N-H+...OOHAu (Supplementary Fig. 22c), [MTBD]N-H+····OH_{Pt} (Supplementary Fig. 22d), [DEMA] N-H+...OH_{Pt} (Supplementary Fig. 22e) and [C₄Him]N-H+...OH_{Pt} (Supplementary Fig. 22f), where the wavefunctions and energy levels of different quantum states are shown in Supplementary Figs. 23-28. The PCET reaction for the transition between vibrational states of reactant (for example, N-H+...OOH_{Au}) and product (for example, H_2O_2) was described, where the exchange current density was proportional to the product of the vibronic coupling squared. Here we assume that the electronic coupling is unchanged for the ORR with different protic cations as the distance between reaction



Fig. 4 | pK_a -dependent interfacial hydrogen-bond structure. In situ ATR-SEIRAS measurement on an ionic-liquid-modified gold and platinum electrodes in 0.1M HClO₄. **a**-**f**, X-H (X = N, O) stretching region of [MTBD][NTf₂]-modified gold (**a**), [DEMA][NTf₂]-modified gold (**b**), [C₄Him][NTf₂]-modified gold (**c**), [MTBD][NTf₂]-modified platinum (**d**), [DEMA][NTf₂]-modified platinum (**e**) and [C₄Him][NTf₂]-modified platinum (**f**). The spectra were acquired at 0.2 V_{RHE} for gold and 0.5 V_{RHE} for platinum. The peak position of the hydrogen-bonded species indicates the strength of the hydrogen bond forming during the ORR process. **g,h**, The relationship between the stretching frequency of the hydrogen-bonding species and the ionic liquid enhancement for ORR catalysed by Au/C (**g**) and Pt/C (**h**), which is defined by $J_{IL-M/C}/J_{M/C}$ (where $J_{IL-M/C}$ is the ORR current density of the ionic-liquid-modified sample and $J_{M/C}$ is the current density of pristine Pt/C or Au/C). Error bars represent standard deviations of at least three independent measurements. The relationship indicates stronger hydrogen bonds would lead to higher ORR activity. The curves only serve as a guide to the eyes.

intermediate (adsorbed OOH and OH) and electron donor (electrode surface, gold and platinum) remains constant⁴. Therefore, we will focus on the effect of the hydrogen-bonding structure on the overall PCET kinetics in this part; the exchange current density is proportional to the product of the vibronic coupling of proton squared (denoted as $S^2_{\mu\nu}$)³, the Boltzmann probability of different proton vibrational states $(P_{\mu})^{3}$ and the Boltzmann probability of overcoming the activation free energy (ΔG^{\dagger}) in Fig. 5b. As summarized in Supplementary Tables 5 and 6, where one or two states dominate the overall kinetics, showing much higher rate constants than others, the differences in ΔG^{\ddagger} of the contributing states of [MTBD]N-H+····OOH_{Au}, [DEMA]N-H+····OOH_{Au} and [C₄Him]N-H+...OOH_{Au} are within 0.05 eV (Supplementary Table 7). Similarly, the differences in ΔG^{\ddagger} (Supplementary Table 8) of the contributing states of [MTBD]N-H+...OH_{Pt}, [DEMA]N-H+...OH_{Pt} and $[C_4Him]N-H^+\cdots OH_{Pt}$ are within 0.04 eV. These results indicate that the effect of ΔG^{\ddagger} on the PCET kinetics is insignificant in this work while the enhancement in the ORR exchange current density mainly resulted from the hydrogen-bonding structure, regulating the tunnelling kinetics of PCET and tuning the pre-exponential factor in the rate constant expression.

ORR activity of gold and platinum by the presence of protic cations with selected pK_a can be attributed to the greater $P_{\mu}S_{\mu\nu}^2$ of protons across the contributing states (Fig. 5e,f). P_{μ} , the Boltzmann probability of contributing quantum states, is shown in Supplementary Tables 7 and 8. $S_{\mu\nu}^2$ was quantified by the integral overlap of proton vibrational wavefunctions between reactant (oxidized state, before electron transfer) and product (reduced state, after electron transfer) (Supplementary Tables 7 and 8), indicating the vibronic coupling of proton through the PCET process. As shown in Fig. 5c and Supplementary Table 7, the proton wavefunction of the product in state 3 for N-H+...OOH_{Au} distributes more on the nitrogen side, which leads to much higher vibronic coupling $(S_{\mu\nu})$ than in the other states, thus the (0,3) transition is the contributing state for the overall kinetics (Supplementary Table 5). This transition accounts for more than 90% of the overall rate constant of $[C_4 Him]N-H^+\cdots OOH_{Au}$ and [MTBD]N–H+…OOH_{Au}, and accounts for 53% of the overall rate constant of [DEMA]N-H+...OOH_{Au}. Another contributing state of [DEMA]N–H⁺···OOH_{Au} is (0,0), which accounts for 35% of the overall rate constant. In Supplementary Table 7, the PCET kinetics is dominated by the vibronic coupling of protons across the ground

Our computational results show that the enhancement in the



Fig. 5 | Hydrogen-bond-dependent PCET kinetics in the ORR. Evaluating the structural effect of interfacial hydrogen bonding by calculating the vibrational wavefunction and energy levels for proton vibrational states of hydrogen-bonded species. **a**, Schematic of the PCET reaction at a hydrogen-bonded interface. The red and blue curves depict proton potential and proton wavefunction (shaded curve) in the ground state of reactant and product as functions of the proton coordinate. The proton is close to the proton donor in the reactant. After the hydrogen-bonded species has obtained an electron from the metal electrode, proton will transfer to the proton acceptor in the product. The reaction kinetics is related to the integral overlap of wavefunctions between the reactant and product (denoted as $S_{\mu\nu}$) and the Boltzmann probability of different vibronic states (denoted as P_{μ}). **b**, The expression of current density shows that J_0 (exchange current density) is proportional to $P_{\mu}S_{\mu\nu\nu}^2$, which is dominated by the hydrogen-bonding structure. $k_{\rm Br}$. Boltzmann constant. **c**,**e**, Schematic depiction of the free energy surface for the PCET reaction in NH⁺…OOH_{Au} (**c**) and NH⁺…OH_{Pt} (**e**). The Marcus parabolas of reactant (red) and product (blue) in the centre frame illustrate the non-adiabatic transitions occurring at the collective solvent coordinates across the intersection (black points) of reactant and product parabolas. Proton potentials and proton wavefunctions in the contributing state of the reactant and product as functions of the proton coordinate are depicted in the left (reactant) and right (product) frames. For NH⁺…OOH_{Au} (**c**), the transition from the reactant ground state to the product third state (0,3) is the contributing state. For NH⁺…OH_{Pt} (**e**), the transition from the reactant first state to the product ground state (1,0) is the contributing state. **d**, f. The $P_{\mu}S_{\mu\nu}$ (light colour) of the contributing state for different ionic liquid cations interacting wit

states of reactant to state 3 of product (0,3), with P_0 close to 1. $P_0S_{03}^2$ and the exchange current density (J_0) for [DEMA]N-H⁺···OOH_{Au} were found to be higher than for [C4Him]N-H+...OOHAu and [MTBD]N-H+...OOH_{Au} in Fig. 5d and Supplementary Tables 7 and 9, which is in agreement with experimental results (Fig. 2). We also note that another contributing state (0,0) of [DEMA]N-H+...OOH_{Au} has higher $P_0 S_{00}^2$ than two other cations as well (Supplementary Table 7), which is consistent with our argument. For the PCET process from N-H⁺ to OH on platinum, the proton wavefunction of reactant in state 1 distributes more on the oxygen side (Fig. 5e) which can generate much higher vibronic coupling in the (1,0) transition state than in (0, 0) to compensate for the decrease in the P_{μ} of state 1 for reactant, leading to the (1,0) transition becoming the contributing state for PCET kinetics in N-H⁺···OH_{Pt}. Since the S_{10} was similar for different ionic liquids in Supplementary Table 8, the PCET kinetics is governed by the P_1 . $P_1S_{10}^2$ and the exchange current

density (J_0) for [MTBD]N⁺-H···OH_{Pt} were found to be the highest, in agreement with experimental exchange current density trends, as shown in Fig. 5f and Supplementary Tables 8 and 10. Therefore, increasing the ORR activity of gold and platinum by the presence of protic cations can be attributed to the greater $P_{\mu}S_{\mu\nu}^2$ of protons across the contributing states, peaking at [DEMA]N-H+...OOH_{Au} with comparable pK_a between [DEMA]N-H⁺ and H₂O₂, and [MTBD]N-H⁺···OH_{Pt} with comparable pK_a between [MTBD]N- H^+ and H_2O_1 , respectively. The predicted J_0 is in good agreement with those measured experimentally (Supplementary Tables 9 and 10). As P_{μ} and $S_{\mu\nu}$ reflect the properties of hydrogen-bond vibronic states between selected protic cations and ORR intermediates, we reason that the kinetics of the PCET-relevant step on gold and platinum can be tuned by altering the hydrogen-bond structures at the interface. This mechanism stands apart from previous studies on homogeneous reaction rates such as nitrogen reduction⁴⁸, hydrogen evolution⁴⁹ and CO₂ reduction⁵⁰, where the pK_a -dependent kinetics has been attributed largely to the changes in chemical potential of proton, electron potential (tuned by the redox potential of the metal centre) and pK_a -dependent activation energy. Therefore, we propose that the stretching frequency and the $P_\mu S_{\mu\nu}^2$ of a hydrogen bond, which describe the vibrational features of intermediates, can be considered as descriptors for PCET kinetics. This study highlights the important role of vibrational features on reaction kinetics and the opportunities for electrolyte and interface tuning to control reaction kinetics.

Conclusions

This study shows that ORR activity forms a volcano relationship with the pK_a of ionic liquids (serving as a proton donor) on the surface of gold and platinum in acid. The optimized pK_a of the proton donor is around 15 and close to the pK_a value of water for platinum, while the optimized pK_a of the proton donor on gold is around 11, close to the pK_a value of H_2O_2 . In situ ATR-SEIRAS provides direct evidence for the red-shifted stretching frequency of X–H with decreasing $\Delta p K_a$, which is associated with enhanced ORR activity. The effect of the hydrogen-bond structure on the kinetics of PCET is examined by the Boltzmann probability (P_u) and vibronic coupling of protons $(S_{\mu\nu})$ in different quantum states. Our results reveal that stronger hydrogen bonds can increase the proton tunnelling kinetics $(P_{\mu}S_{\mu\nu}^2)$ by ~10–10³ times whereas the activation free energy (ΔG^{\ddagger}) of the reaction remains largely unchanged. This work provides compelling evidence for pK_a -dependent hydrogen-bond structures and their impact on the kinetics of proton tunnelling and the rate-limiting PCET of the ORR on platinum and gold, where altering the pK_a of the proton donor at the catalyst surface can change the hydrogen-bonding interaction with ORR intermediates. Our findings highlight opportunities beyond conventional catalyst design strategies of surface electronic structure tuning to control catalytic activity by tuning hydrogen-bond structures and/or solvation environments at the electrified interface.

Methods

Carbon-supported metal (Pt/Au/Ag) catalysts. Pt/C catalysts were supplied by Tanaka Kikinzoku (TKK TEC10E20A), with weight fraction 19%. The gold nanoparticles were synthesized following a reported approach⁵¹. Briefly, tetralin (10 ml), oleylamine (OAm) (10 ml) and HAuCl₄·3H₂O (0.1 g) were mixed at room temperature and magnetically stirred for 10 min under a nitrogen atmosphere to make the precursor solution. Then, a reducing solution of 0.5 mmol TBAB, tetralin (1 ml) and OAm (1 ml) was injected into the precursor solution, and the reaction was carried out in a water-ice bath to maintain the temperature at 2 °C for 1 h. After reaction, the nanoparticles were washed with acetone and collected by centrifugation. The silver nanoparticles were synthesized by a reported one-pot method⁵². Briefly, 150 mg of AgNO₃ was added to 25 ml of a mixture of paraffin and oleylamine (4:1 v/v). The resulting solution was heated under a nitrogen atmosphere at 180 °C for 2h and then at 150 °C for 8h. The nanoparticles were washed with acetone and collected by centrifugation. As-prepared gold and silver nanoparticles and carbon black were dispersed in solvent (1:1 isopropanol/hexane) by a 20 min ultrasonication treatment to synthesize the Au/C catalysts, resulting in 30 wt% gold loading. The products were collected by centrifugation. To remove the residual surfactant, the loaded nanoparticles were heated at 200 °C for 0.5 h under an argon atmosphere.

Synthesis of ionic liquids. $[C_4C_1im][NTf_2]$ (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, CAS no. 174899-83-3) was purchased from Sigma Aldrich. [TMPim][NTf_2] (1,3-bis(2,4,6-trimethylphenyl)imidazolium bis(trifluoromethanesulfonyl)imide) was synthesized by a previously reported anion-exchange reaction⁵³. Li[NTf_2] aqueous solution was added slowly to [TMPim]Br, which also dissolves in water. After the reaction, the ionic liquid formed a separated phase beneath the water phase. The product was washed with ultrapure water, and 0.1 M AgNO₃ added to test for traces of residual Br⁻ in the aqueous layer. The ionic liquid was washed until the AgNO₃ test was negative. The resulting product was dried by high vacuum at 80°C for 24 h. [MTBD][NTf_2] (1,3,4,6,7,8-hexahydro-1-methyl-2*H*-pyrimido[1,2-a]pyrimidinebis(trifluorome thanesulfonyl)imide), [DBU][NTf_2] (2,3,4,6,7,8,9,10-octahydropyrimidol[1,2-a] azepine bis(trifluoromethanesulfonyl)imide), [DEMA][NTf_2] (*N*,*N*'.iettramethylethylenediamine bis(trifluoromethanesulfonyl)imide) and

 $[\rm C_4Him][\rm NTf_2]$ (1-butyl-imidazolium bis(trifluoromethanesulfonyl)imide) were prepared through neutralization reactions in accordance with a previous report⁵⁴. The MTBD, DBU, DEMA, TEMEDA and C₄Him aqueous solutions were added to HNTf₂ solution slowly with cooling by an ice bath. The products formed a separated phase beneath the water phase which was washed by ultrapure water several times and dried under high vacuum at 80 °C for 24 h.

Synthesis of ionic-liquid-modified catalysts. The ionic-liquid-modified catalysts were synthesized by a previously reported protocol²¹. Briefly, 90 mg M/C (M = Pt, Au, 19 wt% TKK Pt/C, as-prepared 30 wt% Au/C) was mixed with 10 ml isopropyl alcohol solution containing a calibrated amount of ionic liquid (corresponding to a final ionic-liquid loading of 16 wt%) with stirring at room temperature. After a 20 min ultrasonic treatment, the solvent was first evaporated under a low-vacuum condition and then dried under high vacuum at 80 °C for 24 h.

Electrochemical characterization. All the electrochemical measurements were performed using a Biologic SP-300 potentiostat with a three-electrode electrochemical system. The working electrode was a glassy carbon rotating disk electrode (0.196 cm²). The slurry was deposited on the working electrode, which consisted of 5 mg M/C (M = Pt, Au) and 5 ml of a mixture of deionized water, isopropyl alcohol and 5 wt% Nafion solution in a ratio of 4:1:0.025 (v/v/v). The loading of platinum was controlled at 20 µg cm⁻² and the loadings of gold and silver were controlled at 40 µg cm⁻². The electrolyte was prepared from Milli-Q water (18 MΩ·cm) and HClO₄ (70%, 99.999% trace metals basis). The saturated calomel electrode potential scale was calibrated with the RHE scale using H₂ electro-oxidation. All measurements were collected under argon or oxygen saturation (ultrahigh-grade purity, Airgas). The specific kinetic activity $(J_k, \text{ mA cm}_{Au \text{ or } Pt}^{-2})$ of Au/C and Pt/C samples was calculated from the Koutecky-Levich equation and the electrochemical surface area was determined by cyclic voltammetry; detailed methods are provided in the Supplementary Information.

In situ ATR-SEIRAS experiments. For the in situ SEIRAS measurements, we used a working electrode comprising a thin (~50 nm) gold or platinum film deposited on a silicon prism (radius 22 mm, Pier optics) by electroless deposition41, The prism was then assembled into a three-electrode cell along with an Ag/ AgCl reference electrode and a platinum wire counter-electrode. The SEIRAS experiments were conducted on a FT-IR Vertex 70 (Bruker) Fourier-transform infrared (FTIR) spectrometer equipped with a mercury-cadmium-telluride detector. The optical path was completely filled with nitrogen gas. The FTIR spectra were acquired in ATR mode using a single-reflection ATR accessory (Vee-Max II, Pike Technologies) at an incident angle of 68°. The spectral resolution was 4 cm⁻¹ and the scan velocity was 7.5 kHz. Each spectrum was measured by superimposing 256 interferograms. During each experiment, oxygen was bubbled through the electrolyte, and the prism surface was then cleaned by cyclic voltammetry between 0 and $1.0 V_{RHE}$. After cleaning, the spectra were collected while applying potentiostatic potentials. All spectra were presented in the form of absorbance according to $\log(I_0/I)$, where I_0 and I are the spectra of the background at the open-circuit potential and at the potentiostatic potential, respectively. Details of the in situ SEIRAS are described elsewhere^{41,55}.

FTIR frequency calculations. The computed vibrational frequency shifts for hydrogen-bonded species were simulated by DFT from the vibrational frequencies of individual ionic liquid cations, and by including the interaction of individual cations with a hydrogen bond from a nearby OH or OOH, in an implicit solvation model (PCM); 2-pentanone (dielectric constant = 15.5) was used as solvent⁵⁶. We used the B3LYP functional and the 6-311++G** basis set, as implemented in the Gaussian (g16) suite⁵⁷. It should be noted that the effects of the metal surface and the applied potential were neglected in these calculations, which should not influence the outcome. In general, these effects can be significant, but the qualitative trends for the vibrational frequencies of ionic liquid cation bonded with OH or OOH should be maintained.

Proton vibration wavefunction calculation. The vibrational wavefunctions and energies were calculated from a series of proton potentials determined for different hydrogen-bonded species calculated from the FTIR frequency, which represent the observed interfacial hydrogen-bond structure at equilibrium states. The one-dimensional proton potentials were scanned using a reported method⁴. Then, the one-dimensional vibrational wavefunctions and energies were calculated from the proton potential by solving the one-dimensional Schrödinger equation numerically using the Fourier Grid Hamiltonian Multiconfigurational Self-Consistent-Field (FGH-MCSCF) method^{3,58}. The Boltzmann probability P_{μ} was calculated from energies of different states, and the $S_{\mu\nu}$ was obtained by integrating the overlap of the reactant and product wavefunctions⁴. The calculation details are presented in the Supplementary Methods. It should be mentioned that to calculate the proton potentials, the models of proton transfer from cations to adsorbed OOH and OH were adopted as an approximation for the ORR on gold and platinum. The effects of the metal surface and the applied potential are neglected in the model.

NATURE CATALYSIS

Data availability

The data supporting the findings of this study are available in the paper and its Supplementary Information. Extra data are available from the corresponding authors on reasonable request.

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References

- 1. Hammes-Schiffer, S. & Stuchebrukhov, A. A. Theory of coupled electron and proton transfer reactions. *Chem. Rev.* **110**, 6939–6960 (2010).
- Weinberg, D. R. et al. Proton-coupled electron transfer. Chem. Rev. 112, 4016–4093 (2012).
- Hammes-Schiffer, S. & Soudackov, A. V. Proton-coupled electron transfer in solution, proteins, and electrochemistry. J. Phys. Chem. B 112, 14108–14123 (2012).
- Horvath, S., Fernandez, L. E., Soudackov, A. V. & Hammes-Schiffer, S. Insights into proton-coupled electron transfer mechanisms of electrocatalytic H₂ oxidation and production. *Proc. Natl Acad. Sci. USA* 109, 15663–15668 (2012).
- Mayer, J. M. Proton-coupled electron transfer: a reaction chemist's view. Annu. Rev. Phys. Chem. 55, 363–390 (2004).
- Koper, M. T. Theory of multiple proton–electron transfer reactions and its implications for electrocatalysis. *Chem. Sci.* 4, 2710–2723 (2013).
- Mora, S. J. et al. Proton-coupled electron transfer in artificial photosynthetic systems. Acc. Chem. Res. 51, 445–453 (2018).
- Viswanathan, V., Hansen, H. A., Rossmeisl, J. & Nørskov, J. K. Unifying the 2e⁻ and 4e⁻ reduction of oxygen on metal surfaces. J. Phys. Chem. Lett. 3, 2948–2951 (2012).
- Shao, M. H. & Adzic, R. R. Spectroscopic identification of the reaction intermediates in oxygen reduction on gold in alkaline solutions. *J. Phys. Chem. B* 109, 16563–16566 (2005).
- Casalongue, H. S. et al. Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode. *Nat. Commun.* 4, 1–6 (2013).
- Dong, J.-C. et al. In situ Raman spectroscopic evidence for oxygen reduction reaction intermediates at platinum single-crystal surfaces. *Nat. Energy* 4, 60–67 (2019).
- 12. Strasser, P. et al. Lattice-strain control of the activity in dealloyed core-shell fuel cell catalysts. *Nat. Chem.* **2**, 454-460 (2010).
- Bligaard, T. & Nørskov, J. K. Ligand effects in heterogeneous catalysis and electrochemistry. *Electrochim. Acta* 52, 5512–5516 (2007).
- 14. Calle-Vallejo, F. et al. Finding optimal surface sites on heterogeneous catalysts by counting nearest neighbors. *Science* **350**, 185–189 (2015).
- Stamenkovic, V. R. et al. Improved oxygen reduction activity on Pt₃Ni(111) via increased surface site availability. *Science* 315, 493–497 (2007).
- 16. Escudero-Escribano, M. et al. Tuning the activity of Pt alloy electrocatalysts by means of the lanthanide contraction. *Science* **352**, 73–76 (2016).
- Snyder, J., Fujita, T., Chen, M. W. & Erlebacher, J. Oxygen reduction in nanoporous metal-ionic liquid composite electrocatalysts. *Nat. Mater.* 9, 904–907 (2010).
- Blizanac, B. B. et al. Anion adsorption, CO oxidation, and oxygen reduction reaction on a Au(100) surface: the pH effect. J. Phys. Chem. B 108, 625–634 (2004).
- Koper, M. T. M. Volcano activity relationships for proton-coupled electron transfer reactions in electrocatalysis. *Top. Catal.* 58, 1153–1158 (2015).
- 20. Chen, C. et al. Highly crystalline multimetallic nanoframes with three-dimensional electrocatalytic surfaces. *Science* **343**, 1339–1343 (2014).
- Zhang, G. R., Munoz, M. & Etzold, B. J. Accelerating oxygen-reduction catalysts through preventing poisoning with non-reactive species by using hydrophobic ionic liquids. *Angew. Chem. Int. Ed.* 55, 2257–2261 (2016).
- 22. Strmcnik, D. et al. The role of non-covalent interactions in electrocatalytic fuel-cell reactions on platinum. *Nat. Chem.* **1**, 466–472 (2009).
- Li, M. F., Liao, L. W., Yuan, D. F., Mei, D. & Chen, Y.-X. pH effect on oxygen reduction reaction at Pt(111) electrode. *Electrochim. Acta* 110, 780–789 (2013).
- 24. Benn, E., Uvegi, H. & Erlebacher, J. Characterization of nanoporous metal-ionic liquid composites for the electrochemical oxygen reduction reaction. *J. Electrochem. Soc.* **162**, H759–H766 (2015).
- 25. Miran, M. S., Yasuda, T., Susan, M. A. B. H., Dokko, K. & Watanabe, M. Electrochemical properties of protic ionic liquids: correlation between open circuit potential for H₂/O₂ cells under non-humidified conditions and ΔpK_a. *RSC Adv.* **3**, 4141–4144 (2013).
- Khan, A., Gunawan, C. A. & Zhao, C. Oxygen reduction reaction in ionic liquids: fundamentals and applications in energy and sensors. ACS Sustain. Chem. Eng. 5, 3698–3715 (2017).
- 27. Higgins, E. M. et al. pK_as of the conjugate acids of N-heterocyclic carbenes in water. Chem. Commun. 47, 1559–1561 (2011).

- Kaupmees, K., Trummal, A. & Leito, I. Basicities of strong bases in water: a computational study. Croat. Chem. Acta 87, 385–395 (2014).
- Otake, Y., Nakamura, H. & Fuse, S. Rapid and mild synthesis of amino acid N-carboxy anhydrides: basic-to-acidic flash switching in a microflow. *React.* Angew. Chem. Int. Ed. 130, 11559–11563 (2018).
- Spialter, L. & Moshier, R. W. Amines IV The base strengths of tetramethylated 1,2-ethanediamines. J. Am. Chem. Soc. 79, 5955–5957 (1957).
- Tehan, B. G. et al. Estimation of pK_a using semiempirical molecular orbital methods. Part 2: application to amines, anilines and various nitrogen containing heterocyclic compounds. *Quant. Struct.-Act. Relat.* 21, 473–485 (2002).
- Wang, J., Markovic, N. & Adzic, R. Kinetic analysis of oxygen reduction on Pt (111) in acid solutions: intrinsic kinetic parameters and anion adsorption effects. J. Phys. Chem. B 108, 4127–4133 (2004).
- Shinozaki, K., Zack, J. W., Richards, R. M., Pivovar, B. S. & Kocha, S. S. Oxygen reduction reaction measurements on platinum electrocatalysts utilizing rotating disk electrode technique. *J. Electrochem. Soc.* 162, F1144–F1158 (2015).
- 34. Ford, D. C., Nilekar, A. U., Xu, Y. & Mavrikakis, M. Partial and complete reduction of O₂ by hydrogen on transition metal surfaces. *Surf. Sci.* 604, 1565–1575 (2010).
- Chevalet, J., Rouelle, F., Gierst, L. & Lambert, J. P. Electrogeneration and some properties of the superoxide ion in aqueous solutions. *J. Electroanal. Chem. Inter. Electrochem.* 39, 201–216 (1972).
- Costentin, C., Evans, D. H., Robert, M., Saveant, J. M. & Singh, P. S. Electrochemical approach to concerted proton and electron transfers. Reduction of the water-superoxide ion complex. *J. Am. Chem. Soc.* 127, 12490–12491 (2005).
- Li, X. & Gewirth, A. A. Oxygen electroreduction through a superoxide intermediate on bi-modified Au surfaces. J. Am. Chem. Soc. 127, 5252–5260 (2005).
- Wakisaka, M., Suzuki, H., Mitsui, S., Uchida, H. & Watanabe, M. Increased oxygen coverage at Pt-Fe alloy cathode for the enhanced oxygen reduction reaction studied by EC-XPS. J. Phys. Chem. C. 112, 2750–2755 (2008).
- Brzezinski, B. & Zundel, G. Formation of hydrogen-bonded chains between strong N-base and N-H acids—a FTIR study. J. Mol. Struct. 446, 199-207 (1998).
- Moschovi, A. M., Ntais, S., Dracopoulos, V. & Nikolakis, V. Vibrational spectroscopic study of the protic ionic liquid 1-H-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. *Vib. Spectrosc.* 63, 350–359 (2012).
- Ataka, K.-I. et al. Reorientation of water molecules at an electrode/electrolyte interface studied by surface-enhanced infrared absorption spectroscopy. J. Phys. Chem. 100, 10664–10672 (1996).
- Nakamoto, K., Margoshes, M. & Rundle, R. E. Stretching frequencies as a function of distances in hydrogen bonds. J. Am. Chem. Soc. 77, 6480–6486 (1955).
- 43. Gilli, P., Pretto, L., Bertolasi, V. & Gilli, G. Predicting hydrogen-bond strengths from acid-base molecular properties. The pK_a slide rule: toward the solution of a long-lasting problem. Acc. Chem. Res. 42, 33-44 (2009).
- 44. Jusys, Z., Schnaidt, J. & Behm, R. J. O₂ reduction on a Au film electrode in an ionic liquid in the absence and presence of Mg⁽²⁺⁾ ions: product formation and adlayer dynamics. *J. Chem. Phys.* **150**, 041724 (2019).
- Cheng, H.-W. et al. Characterizing the influence of water on charging and layering at electrified ionic-liquid/solid interfaces. *Adv. Mater. Interfaces* 2, 1500159 (2015).
- 46. Liu, Y.-P. & Newton, M. D. Reorganization energy for electron transfer at film-modified electrode surfaces: a dielectric continuum model. *J. Phys. Chem.* **98**, 7162–7169 (1994).
- Maurel, P. Relevance of dielectric constant and solvent hydrophobicity to the organic solvent effect in enzymology. J. Biol. Chem. 253, 1677–1683 (1978).
- Chalkley, M. J., Del Castillo, T. J., Matson, B. D. & Peters, J. C. Fe-mediated nitrogen fixation with a metallocene mediator: exploring pK_a effects and demonstrating electrocatalysis. J. Am. Chem. Soc. 140, 6122–6129 (2018).
- Kilgore, U. J. et al. [Ni(PPh₂NC₆H₄X₂)₂]²⁺ complexes as electrocatalysts for H₂ production: effect of substituents, acids, and water on catalytic rates. J. Am. Chem. Soc. 133, 5861–5872 (2011).
- Margarit, C. G., Schnedermann, C., Asimow, N. G. & Nocera, D. G. Carbon dioxide reduction by iron hangman porphyrins. *Organometallics* 38, 1219–1223 (2018).
- 51. Peng, S. et al. A facile synthesis of monodisperse Au nanoparticles and their catalysis of CO oxidation. *Nano Res.* 1, 229-234 (2008).
- Chen, M. et al. Silver nanoparticles capped by oleylamine: formation, growth, and self-organization. *Langmuir* 23, 5296–5304 (2007).
- 53. Huddleston, J. G. et al. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green. Chem.* **3**, 156–164 (2001).
- 54. Nakamoto, H. & Watanabe, M. Bronsted acid-base ionic liquids for fuel cell electrolytes. *Chem. Commun.* **24**, 2539–2541 (2007).

- Miki, A., Ye, S. & Osawa, M. Surface-enhanced IR absorption on platinum nanoparticles: an application to real-time monitoring of electrocatalytic reactions. *Chem. Commun.* 14, 1500–1501 (2002).
- 56. Frisch, M. et al. Gaussian 09 Revision D. 01 (Gaussian, 2009).
- Laury, M. L., Carlson, M. J. & Wilson, A. K. Vibrational frequency scale factors for density functional theory and the polarization consistent basis sets. *J. Comput. Chem.* 33, 2380–2387 (2012).
- Webb, S. P. & Hammes-Schiffer, S. Fourier grid Hamiltonian multiconfigurational self-consistent-field: a method to calculate multidimensional hydrogen vibrational wavefunctions. *J. Chem. Phys.* 113, 5214–5227 (2000).

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Author contributions

Y.S.-H. and T.W conceived the idea and designed the experiments. T.W. carried out experiments on catalyst synthesis, electrocatalytic tests and data analysis. Y.Z. and T.W. performed the in situ surface-enhanced FTIR spectroscopy measurements. Y.Z. and T.W performed the DFT calculations and analysis. T.W. and B.H. analysed the electrochemical data. B.C. synthesized nanoparticles. R.R.R., L.G. and S.-G.S. participated in the discussion and interpretation of experimental and theoretical data. Y.S.-H. and T.W. wrote the manuscript. All of the authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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