Supporting Information
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Adsorbed Intermediates in Oxygen Reduction on Platinum Nanoparticles Observed by In situ IR Spectroscopy

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Abstract: The sluggish kinetics of oxygen reduction to water remains a significant limitation in the viability of proton exchange membrane fuel cells, yet details of the four electron oxygen reduction reaction remain elusive. Here we apply in situ infrared spectroscopy to probe surface chemistry of a commercial carbon-supported Pt nanoparticle catalyst during oxygen reduction. Infrared spectra show potential dependent appearance of adsorbed superoxide and hydroperoxide intermediates on Pt. This strongly supports an associative pathway for oxygen reduction. Analysis of the adsorbates alongside the catalytic current suggests that another pathway must also be in operation, consistent with a parallel dissociative pathway.

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Experimental Procedures

(i) Catalyst preparation:
For all electrochemical and in situ spectroelectrochemical measurements carbon supported Pt catalyst (60 wt. % Pt on Vulcan XC-72R carbon, HiSPEC 9000, Alfa Aesar) was used. 10 mg mL^{-1} Pt/C catalyst ink was prepared in ultrapure water (18.2 MΩ cm, milliQ) and was ultra-sonicated for at least 1 h before every experiment. For control experiments, Vulcan carbon (XC-72R) and unsupported Pt black (HiSPEC 1000, Alfa Aesar) suspensions were prepared in a similar manner as mentioned for Pt/C catalyst. Acid solutions (0.1 M $HClO_4$, Sigma Aldrich) were prepared using ultrapure water. 99.9 % D_2O (Sigma) and $^{18}O_2$ (99 % purity, CK Isotopes) were used for isotope labelled experiments. Anhydrous $NaClO_4$ (Alfa Aesar) was used to prepare 0.1 M $NaClO_4$ in D_2O solution with pD = 1.

(ii) Details of spectroelectrochemical experiments:
For IR experiments, a diamond-like carbon 'DLC' (Neocoat SA, Switzerland) was coated onto a Si wafer (Crystal GmbH, Germany) to prepare the internal reflection element (IRE), and this was then cut to 5×8×1 mm^3 and polished to a 39˚ angle of incidence at both the short edges to provide 5 reflections on the top face. The DLC-coated IRE was ultra-sonicated for 1 min with 30 % conc. H_2SO_4 followed by rinsing with deionized water before every experiment. After cleaning, the IRE was placed in the groove of the baseplate of the spectroelectrochemical cell made up of polyether ether ketone (PEEK) which was designed and built in house. Silicone glue (SE4486CV, Dow Corning) was used to seal all the edges of the IRE sitting on the baseplate. 10 µL of 10 mg mL^{-1} catalyst ink was drop cast on the IRE and dried under air at room temperature. A sheet of carbon paper (TGP-H-030, Toray Industries, Inc.) was placed on top of the catalyst layer in order to make the electrical contact during electrochemical potential application. The top part of the cell has 5 holes for a working electrode (1 mm glassy carbon rod, Alfa Aesar), a reference electrode (Ag/AgCl in 3 M KCl, BAS Inc.), a counter electrode (Pt gauze, Goodfellow) and electrolyte inlet and outlet. The top part of the cell was screwed onto the PEEK baseplate containing the catalyst film on the IRE. The spectroelectrochemical cell assembly was then mounted on an ATR mirror unit (modified from GladiATR, PIKE Technologies). An Agilent Cary 680 FTIR spectrometer with a liquid N_2 cooled HgCdTe detector and a spectral resolution of 4 cm^{-1} was used to record IR spectra. Electrochemical potential application was controlled by a potentiostat (Metrohm Autolab, PGSTAT128N) during recording of IR spectra. IR spectra were collected in kinetics mode every 1 s and co-added, with simultaneous onset of electrochemical cyclic voltammetry triggered by the potentiostat. IR spectra recorded at the initial potential were used as a reference to calculate absorbance at other potentials. Solutions were saturated either with O_2 for ORR or with Ar for inert conditions and flowed into the cell using a peristaltic pump (flow rate: 30 mL min^{-1}). All electrochemical potentials mentioned here are reported with respect to the standard hydrogen electrode (SHE) as ($E_{SHE} = E_{Ag/AgCl} + 0.21$ V).

(iii) ATR-IR cell: For ATR-IR experiments coupled to electrochemistry, a modified spectroelectrochemical cell previously used for metal/ enzyme catalysis was used.[1,2] Finely dispersed Pt/C catalyst was drop cast (film thickness ca 2 µm) onto a DLC-coated Si IRE (Figure S1). Porous carbon paper was placed on top of the catalyst layer for the electrical contact. The benefit of our approach is that the inlet for electrolyte is situated very near to the carbon paper in contact with Pt/C catalyst from the top. This creates a flow field of electrolyte surrounding the catalyst layer which works similar to rotating disk electrode mechanism to avoid any mass transport limitation. During ORR experiments in the spectroelectrochemical cell, the flow rate of electrolyte was increased until there was no more increase in the electrochemical current. The reference electrode was placed in a separate compartment outside of the cell, connected via a narrow diameter capillary to the working electrode compartment, similar to a Luggin capillary. Since diffusion through this capillary is slow, no leakage of the chloride ion from the reference electrode into the working electrode compartment is expected within the short duration of the experiment.

The Pt catalyst layer was electrochemically cleaned by applying E = +0.01 to +1.21 V at 50 mV s^{-1} for 30 cycles in 0.1 M $HClO_4$ prior to in situ experiments.[3] The reference potential is chosen just before the onset of ORR to visualize the formation of ORR intermediates with negative going potentials. We have chosen here E < 1 V potential window for our ORR study as carbon particles undergo corrosion at higher potentials in acid media.[4]

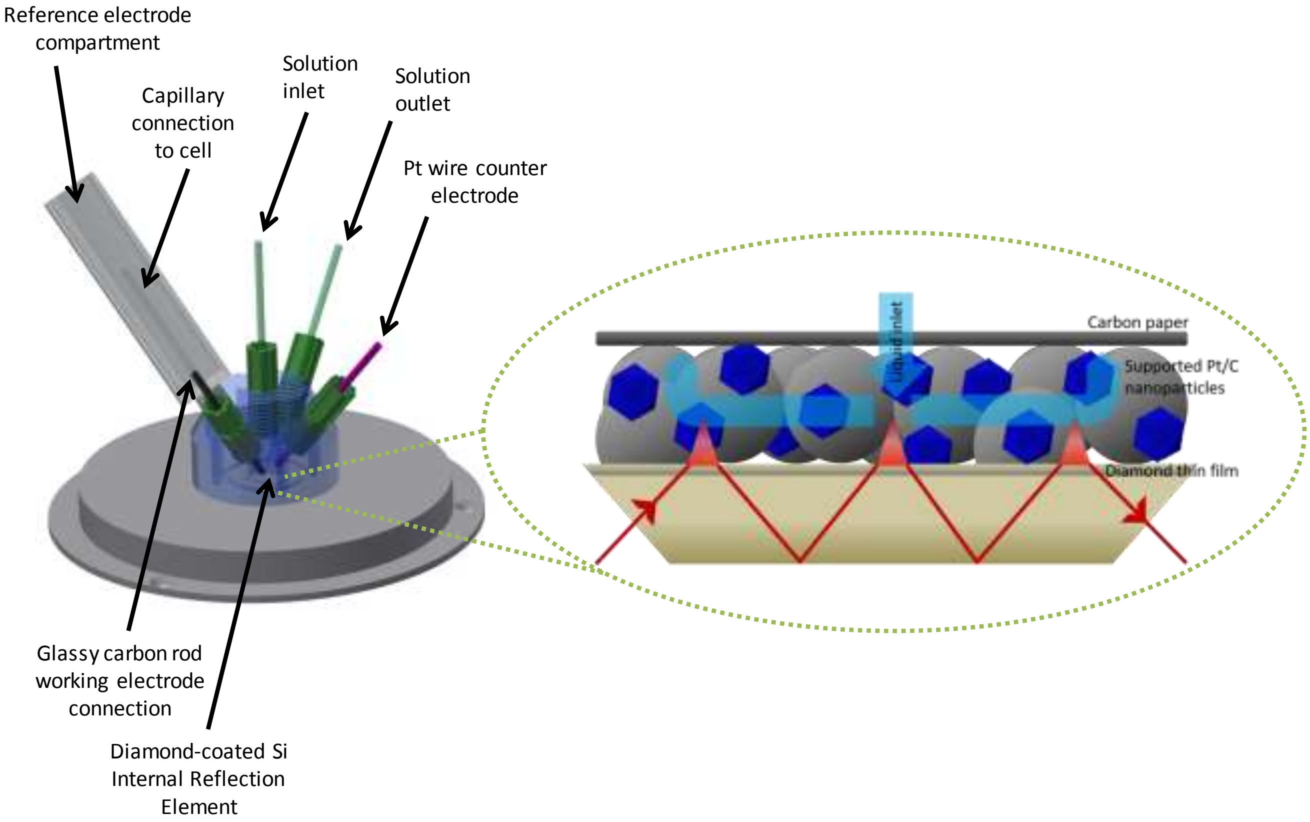

Figure S1 Schematic diagram of the electrochemical ATR-IR technique used for the study of ORR at supported Pt/C nanoparticles in 0.1 M $HClO_4$ solution.

Results and Discussion

S2. Control experiment with carbon support or unsupported Pt nanoparticles

Figure S2a shows the ATR-IR experiment of a Vulcan thin film under O_2 saturated 0.1 M $HClO_4$ solution. IR results show 2 peaks at 1030 cm^{-1} and 1114 cm^{-1} due to adsorbed and solution perchlorate species, respectively, and 2 peaks at 1330 cm^{-1} and 1435 cm^{-1} due to carbon surface functionalities.

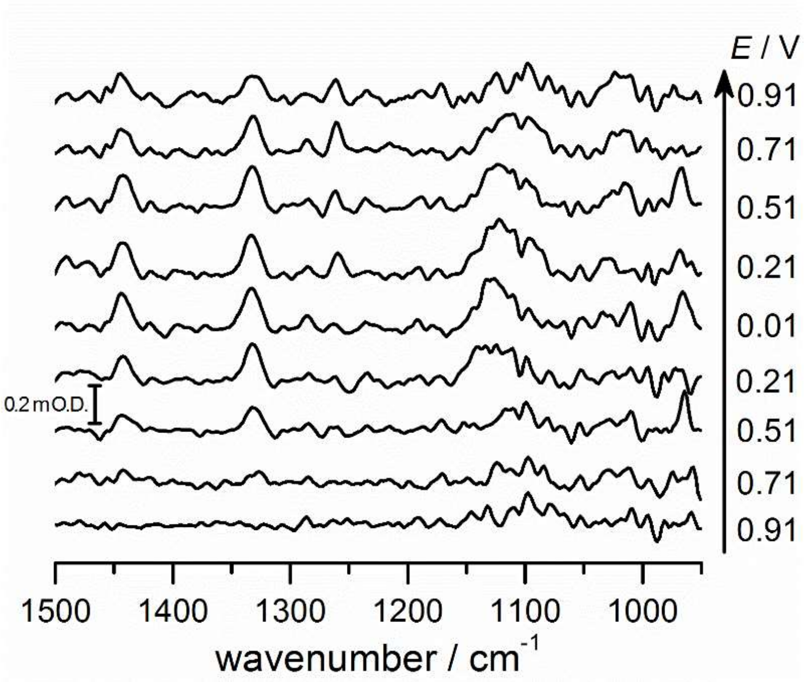

Figure S2a ATR-IR spectra of supported carbon in 0.1 M $HClO_4$ solution saturated with O_2 at different applied potentials during ORR.

Figure S2b shows the ATR-IR experiment of an unsupported Pt (Pt black) thin film under O_2 saturated 0.1 M $HClO_4$ solution. Similar experimental conditions were used as for the Pt/C experiment shown in Figure 1. The dashed lines indicate the wavenumber positions of the oxygenic species observed for Pt/C in Figure 1, and show that similar peaks are observed for Pt black, although it is difficult to assign exact wavenumber positions for the species on Pt black due to lower S/N ratio on the unsupported catalyst. Peaks are also observed on Pt black at lower wavenumber consistent with adsorbed and solution perchlorate species.

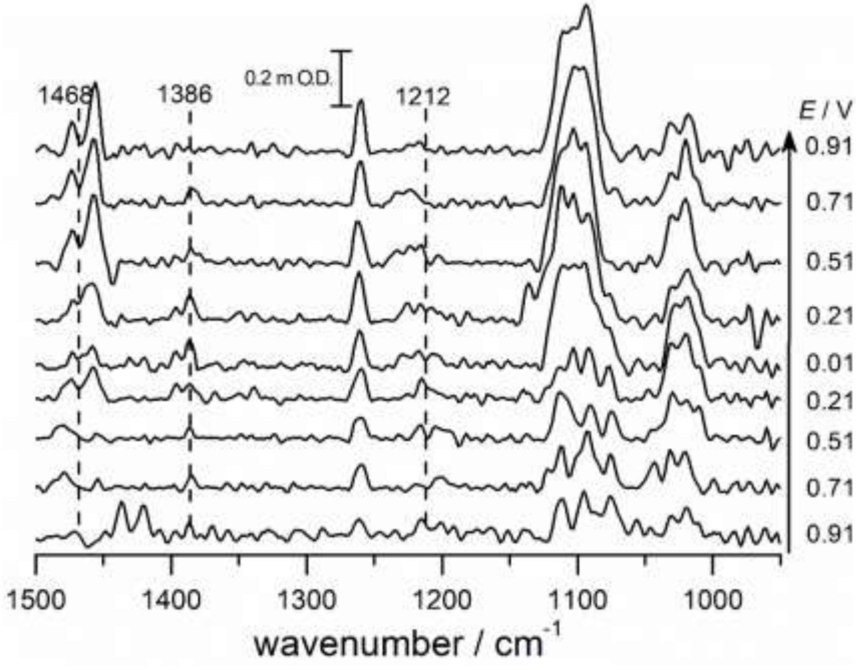

Figure S2b ATR-IR spectra of unsupported Pt catalyst in 0.1 M $HClO_4$ solution saturated with O_2 at different applied potentials during ORR.

S3. Isotope labelled experiments

(i) with $^{18}O_2$: The solution in the outside reservoir and ATR-IR cell with the Pt/C catalyst layer was first saturated and purged with Ar gas before starting the $^{18}O_2$ experiment to avoid any contamination from atmospheric $^{16}O_2$.
The IR spectrum during $^{18}O_2$ experiment at *E*=0.01 V is compared with the corresponding IR spectrum from the $^{16}O_2$ experiment (Figure S3a). It shows that the peak at 1212 cm^{-1} due to adsorbed superoxide (OOH_{ad}) in $^{16}O_2$ medium is shifted to 1164 cm^{-1} in $^{16}O_2$ medium.

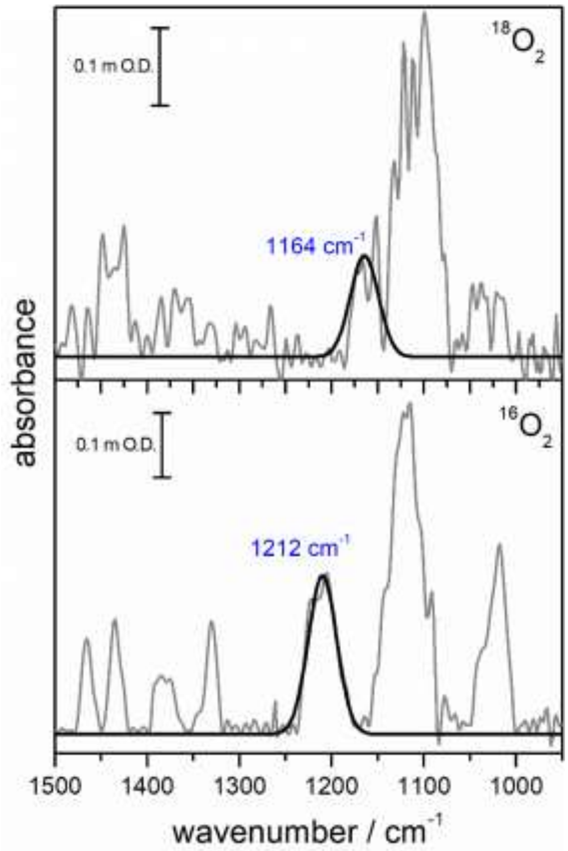

Figure S3a Comparison of IR spectra at Pt/C catalyst during ORR with exchange of isotopic oxygen ($^{18}O_2$) and $^{16}O_2$ at *E*=0.01 V in 0.1 M $HClO_4$ solution.

(ii) with deuterated ClO_4^- solution:
The IR spectrum at *E*=0.01 V during ORR is compared with the deuterated ClO_4^- medium (Figure S3b). For the experiment, anhydrous $NaClO_4$ was used in D_2O solution saturated with O_2 gas at pD = 1. The peak at 1386 cm^{-1} in $HClO_4$ medium is absent in deuterated ClO_4^- medium.

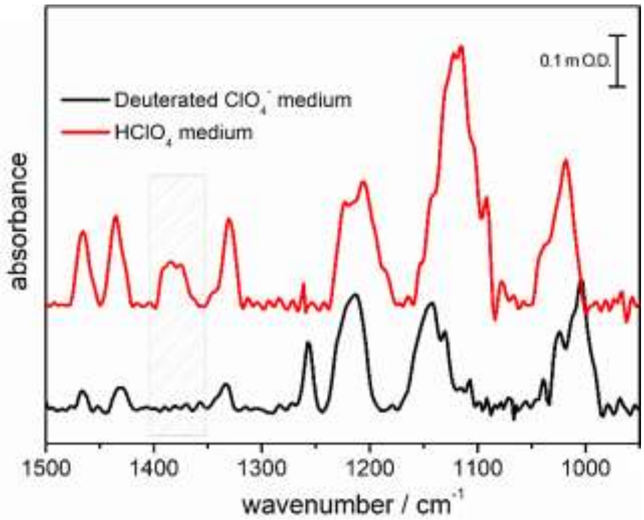

Figure S3b Comparison of IR spectra of the 1386 cm^{-1} peak during ORR on Pt/C catalyst at *E*=0.01 V in 0.1 M $HClO_4$ and deuterated ClO_4^- media.

S4. Details of fitting parameters used for the IR spectra

The IR spectra obtained from in situ spectroelectrochemical experiments were first baseline corrected using OriginPro 2017 software. The peaks at 1212 cm^{-1} and 1386 cm^{-1} were fitted together using Gaussian functions without fixing any parameters. The same procedure was applied to all the IR spectra for ORR of Pt/C catalyst at different potentials and also for the $^{18}O_2$ experiment. For IR spectra under an Ar atmosphere, only baseline correction of the spectra was applied. The baseline corrected spectra with the corresponding fitted peaks at 1212 cm^{-1} and 1386 cm^{-1} are presented in Figure S4.

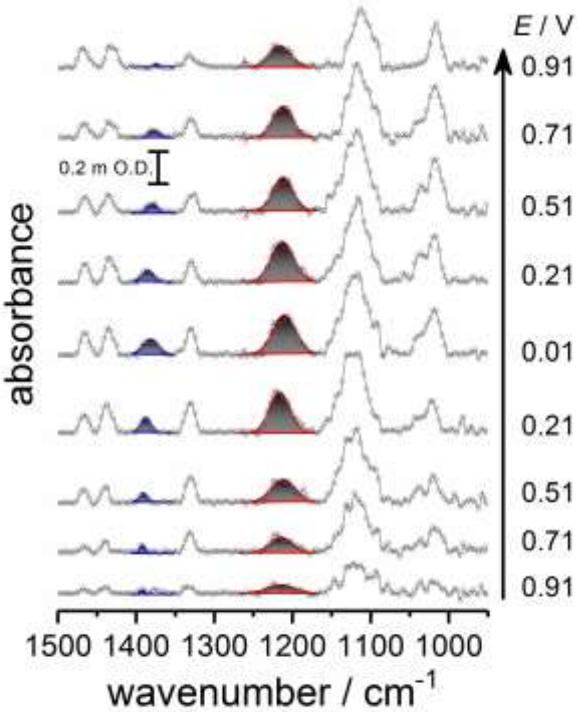

Figure S4 Baseline corrected ATR-IR spectra during ORR at Pt/C catalyst in 0.1 M $HClO_4$ solution with corresponding Gaussian fitting of 1212 cm^{-1} and 1386 cm^{-1} modes.

References

1. R. Hidalgo, P. A. Ash, A. J. Healy, K. A. Vincent, *Angew. Chemie Int. Ed*. 2015, 54, 7110–7113
2. I. J. McPherson, P. A. Ash, R. M. J. Jacobs, K. A. Vincent, *Chem. Commun*. 2016, 52, 12665–12668
3. F. Maillard, E.R. Savinova, P.A. Simonov, V. I. Zaikovskii, U. Stimming, *J. Phys. Chem. B*, 108, 46, 17893-17904
4. P.L. Antonucci, F. Romeo, M. Minutoli, E. Alderucci, N. Giordano, *Carbon* 1988, 26, 197–203