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In situ Investigation of Dissociation and Migration Phenomena at the Pt/Electrolyte Interface of an Electrochemical Cell

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Electronic Supplementary information

SI1. Influence of the cell bias on the apparent binding energy

Application of a voltage between the working (WE) and the counter (CE) electrodes is expected to result in the BE shift (ΔBE) in accordance with equation S1:

$$\Delta BE = BE - BE_{OCV} = -e(V_{WE-CE} - iR - \eta_{CE}) \quad \text{(Eq S1)}$$

Here i is current, BE_{OCV} is the BE value at the open circuit voltage, R is the electrical resistance of the membrane-electrode assembly, and η_{CE} is overpotential at the counter electrode (i.e. the difference between the actual and the equilibrium potential value). The experiments showed that either the increase of the water vapor pressure (from 0 to 0.3 mbar) or the increase of the temperature (from room temperature to 180°C) resulted in a decrease of R.

SI2. Contribution of O from polymer membrane and O from Pt oxides to the overall O 1s XP peak

Contribution of polymer membrane species to the O 1s peak:

C 1s and O 1s spectra recorded over an undoped polymer membrane (before imbibing it with PA) were used as a reference in order to estimate the relative contribution in the O 1s peak of oxygen species derived from the membrane as compared to those of the PA. The O:C peak area ratio for the undoped membrane was equal to 0.17±0.2 while in case of PA imbibed membrane at 0 V this ratio was 3.0±0.2. Therefore one can assume that membrane-derived oxygen species contribute less than 6 % to the overall O 1s signal.

Contribution of PtO_x species to the O 1s peak:

In order to estimate the contribution of the oxidized Pt species in the O 1s peak we have used the following procedure: first, the amount of oxidized Pt was determined by numerical subtraction of the Pt 4f spectrum recorded at OCV from spectra recorded at 1.3 and 1.6 bias voltages, as shown in figure S1 (left). Then, the upper bound for the amount of oxygen corresponding to oxidized Pt was estimated assuming a Pt:O stoichiometry 1:2, taking into account the electron photoinization cross sections and differences in the photon flux using the following equation:

$$\frac{I_{PtO_2}/I_{Pt}^{\infty}}{I_O/I_O^{\infty}} = \frac{1}{2}$$

Here I_{PtO_2} is the experimental intensity (in Counts Per Second) of the Pt 4f peak corresponding to oxidized Pt (PtO_2) estimated by the subtraction procedure shown in fig. S1 (left). I_{Pt}^{∞} and I_O^{∞} are the normalization factors, and I_O the expected intensity contribution of the O 1s component due to platinum oxide. This procedure gave an estimated contribution of Pt oxide-related species which did not exceeds 5 % of the overall O 1s peak signal (3.7 % for 1.3V and 4.4 for 1.6V). A characteristic O 1s spectrum (at 1.6 V) after deconvolution taking into account a O 1s component due to the platinum oxide contribution to the overall O 1s spectrum is shown in S1 (right):

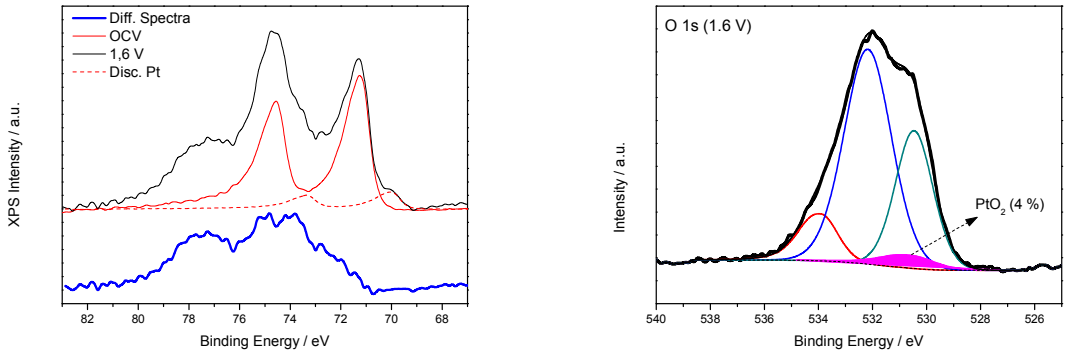

Figure S1. *Left* : Black – Pt4f spectrum collected at 1.6 V bias. Red solid line - Pt 4f spectrum collected at the OCV. Blue - the contribution of the ionic (oxidized) Pt species to the overall Pt 4f spectrum obtained through subtraction of the metallic Pt species (spectrum taken at the OCV) from the spectrum taken at 1.6 V. Red dashed line shows the contribution of disconnected metallic Pt particles. *Right*: Suggested O 1s peak deconvolution including a O 1s component due to the ionic Pt (PtO_2) species. In order to select the binding energy of the O 1s component resulting from PtO_x species, literature values were used, while the intensity of the peak was estimated as described above.

SI3. P/O atomic ratio

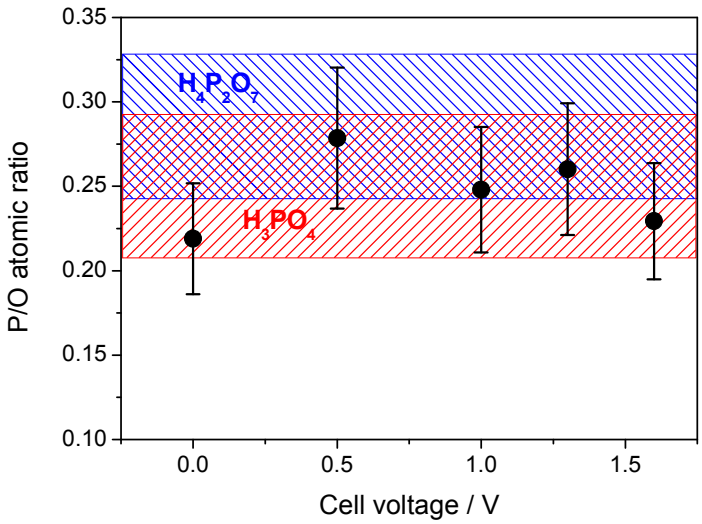

Figure S2. The P:O atomic ratio calculated from *in situ* NAPXPS spectra as a function of the cell voltage. Red- and blue-hatched intervals correspond to the P:O atomic ratio of H_3PO_4 (0.25 ±0.04) and $H_4P_2O_7$ (0.29±0.04), respectively (estimated error of ±15%).

SI4. DFT Calculations

Table S1. BE shifts calculated with the DFT method

Molecule/ion	Functional group	O1s BE shift * /eV
	P=O	0
H_3PO_4	P-O-H	2.0-2.1
H_2O	H_2O	1.2
H_3PO_4	P=O	0.0
	P-O-H	2.3
H-bonded (Figure S2-a))	P=O--H	1.1±0.1
	P-O-H--O	1.6±0.1
$H_3PO_4 + H_2O$	P-OH	2.3
	P=O--H_2O	0.47
H-bonded (Figure S2-b))	P-OH--H_2O	1.8
	H_2O	1.6
$H_4P_2O_7$	P=O	0
	P-O-H	2.1
	P-O-P	2.3
$H_4P_2O_7$	P-O-H	2.2-2.3
	P-O-P	2.3
	P=O--H	1.0
	P-O-H---O	1.6
$H_4P_2O_7 + H_2O$	P-O-P	2.3
	P=O--H	0.5
	P-OH--O	1.6-2.0
	H_2O	1.8
$H_2PO_4^-$ or $H_3P_2O_7^-$	$P-O^-$	-0.2 - 0
	P-OH	2.2
$H_2PO_4^- + H_2O$	P-OH	2.3
	P=O---H_2O	0.3
H-bonded (Figure S2-c))	P-OH---H_2O	1.65
	H_2O	2.02
$H_2PO_4^-$ chemisorbed on Pt	Pt-O-P	1.3
	P-OH	2.2
HPO_4^{2-} chemisorbed on Pt	P-OH	2.2
	Pt-O-P	1.4
PO_4^{3-} chemisorbed on Pt	P=O	0.15
	Pt-O-P	1.80
$H_4P_2O_7$ chemisorbed on Pt	P=O	0.28
	P-OH	2.20
	P-O-P	2.20
	Pt-O-P	2.20
H_3O^+	$O-H^+$	8
$H_4PO_4^+$	$O-H^+$	8
$H_4PO_4^+$ chemisorbed on Pt	Pt-O-P	3 to 2 eV depending on the orientation of the ion relative to the Pt surface

*O1s BE shift is referred to O of P=O of a H_3PO_4 molecule in the gas phase.

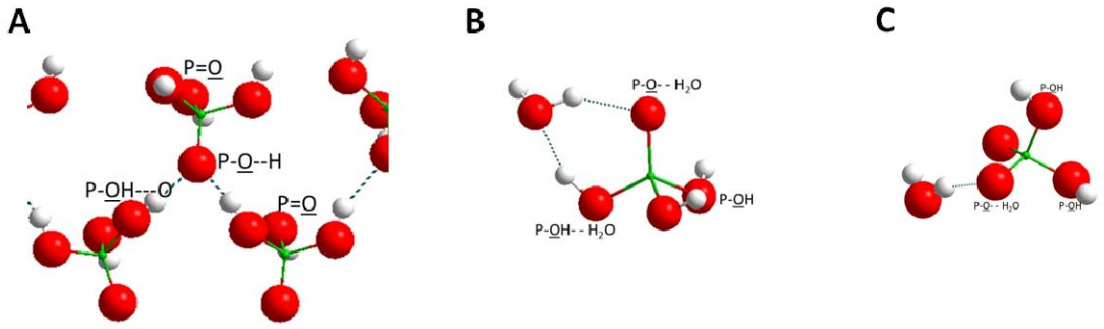

Figure S3: Optimized configurations obtained using the DFT calculations for A) H_3PO_4 molecules in a H-bonded network, B) H_3PO_4 H-bonded with water, C) $H_2PO_4^-$ H-bonded with water.

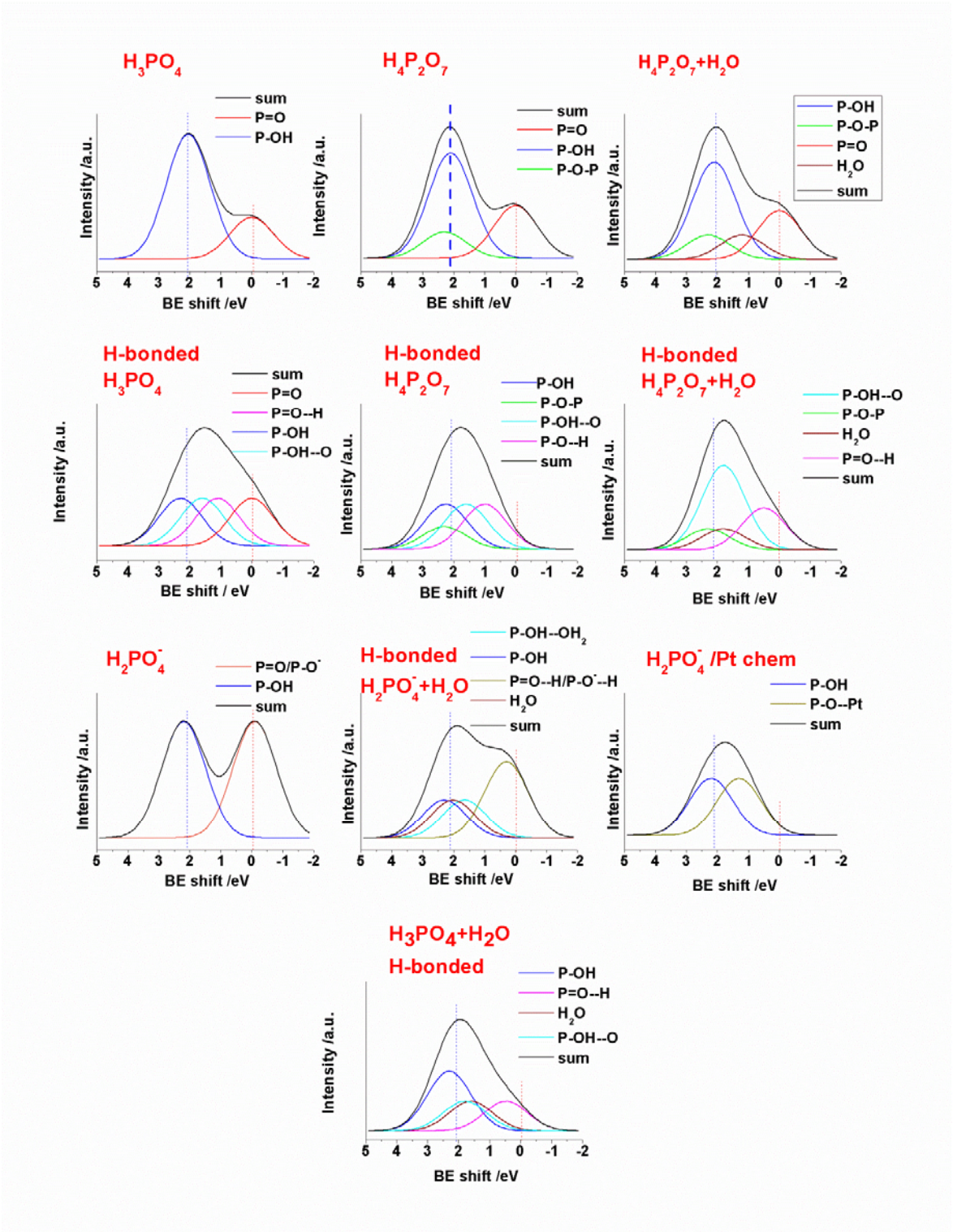

Figure S4. PE spectra simulated for various molecular configurations using BE shifts calculated with the DFT. As the first approximation spectra were simulated assuming Gaussian peak shape. Red and blue dashed lines mark positions of the O1s peak characteristic for P=O and P-OH groups of H_3PO_4 in the gas phase.

SI5. Variation of the Pt/P atomic ratio with the cell voltage: response to the voltage bias reversal

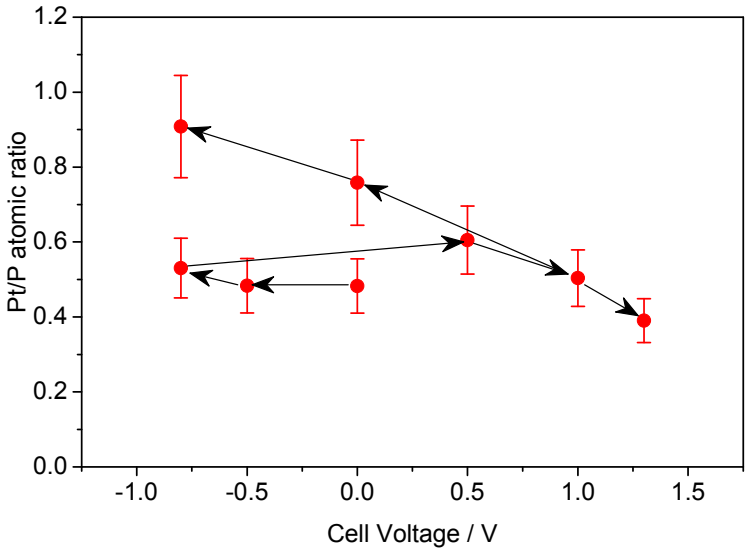

Figure S5. Evolution of the Pt/P atomic ratio with the cell voltage. The arrows show the direction of the potential cycling. The figure shows a decrease of the Pt/P atomic ratio upon application of the positive voltage bias, and its increase upon bias reversal. Temperature is 180°C and water vapor pressure is 0.3 mbar. Kinetic energy of photoelectrons is equal to 580 eV.