Supporting Information

Unveiling N-protonation and anion-binding effects on Fe/N/C-catalysts for O₂ reduction in PEM fuel cells

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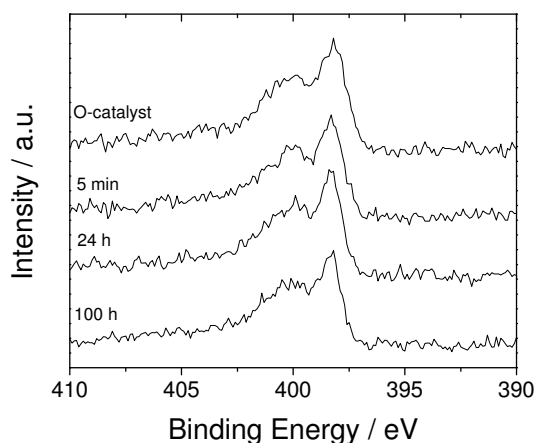Hahn-Meitner-Platz 1, D-14109, Berlin, Germany

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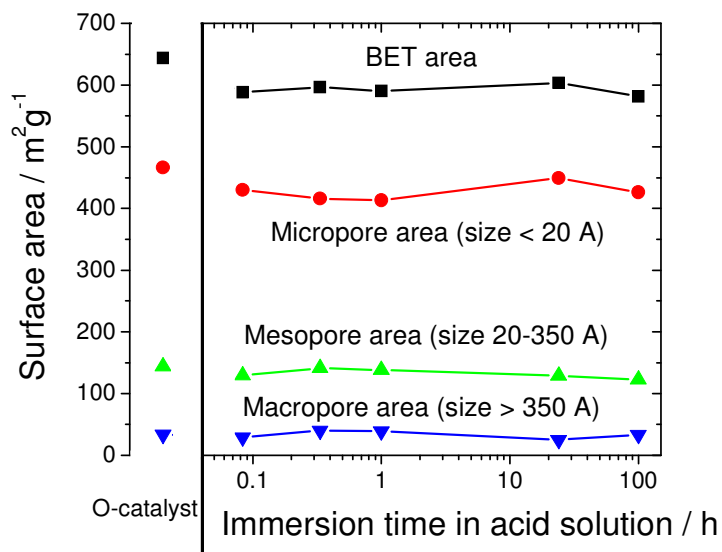
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Figure S1A. N_{1s} XPS-spectra of the original and acid-washed catalysts for various immersion times in a pH 1 H_2SO_4 solution

**Figure S1B. Surface areas of acid-washed catalysts vs. immersion time in a pH 1 H_2SO_4-solution**

The surface areas were estimated from the BET equation and from the fitting of the N_2-adsorption isotherms obtained using Autosorb-1 surface area analyzer from Quantachrome instruments, with the Quenched Solid Density Functional Theory (slit-pore geometry) available in the ASWin software.
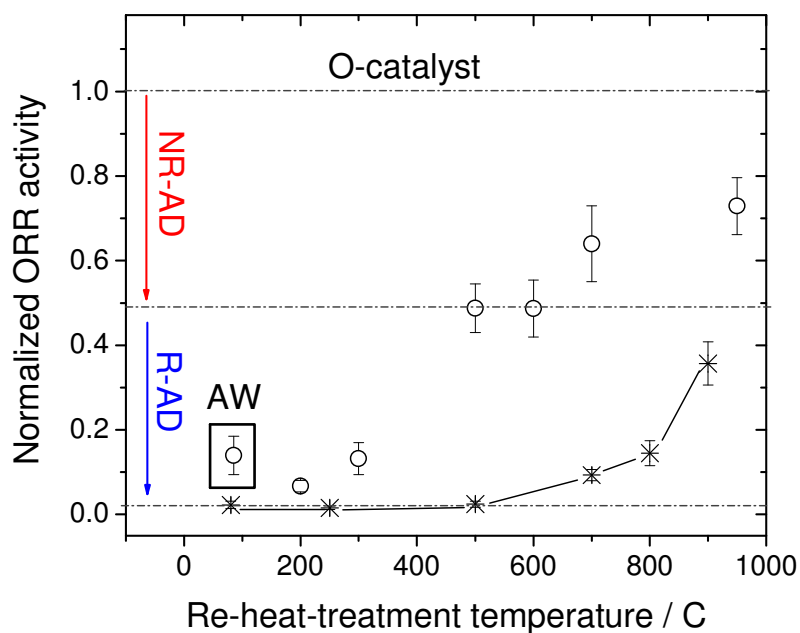
Figure S2. Activity recovery by re-heat-treatment in Ar of catalysts acid-washed in 0.1 M HClO₄

Normalized activity based on that of the original catalyst (O-catalyst) vs. re-heat-treatment temperature in argon, as measured in RDE (open circles, electrolyte pH 1 H_2SO_4-solution).

The acid-washing was performed in a pH 1 HClO₄-solution for 24 h, then the powder was filtered, rinsed and dried at 85°C overnight in air. Several aliquots of the acid-washed catalyst (AW-catalyst) were re-heat-treated in argon at various temperatures for 1 h. The initial activity of the O-catalyst was 2.3 A g^{-1} in RDE. Several aliquots of a test precursor initially free of active sites (see Methods) were heat-treated in argon at various temperatures for 1 h (asterisks) in order to determine the minimum temperature required for catalytic-site formation.
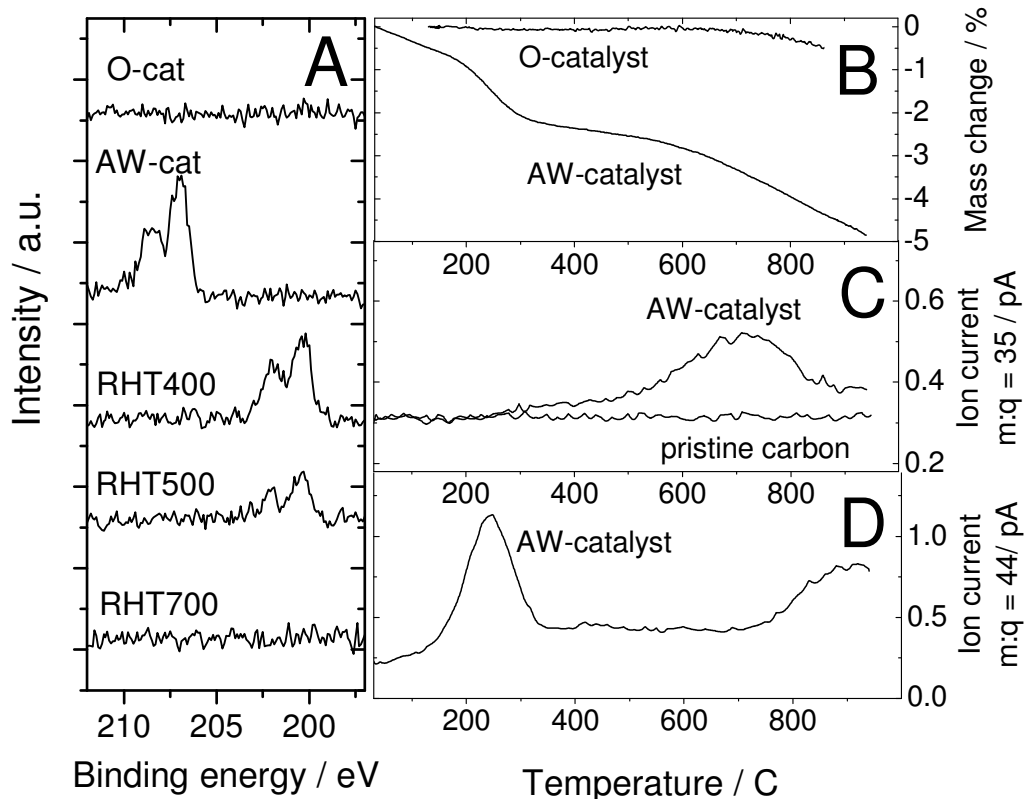
Figure S3. Identification of surface species linked to activity decay upon acid washing in 0.1 M HClO₄

(A) X-ray photo-electron spectra of Cl_{2p} for the original catalyst (O-cat), acid-washed catalyst (AW-cat) and aliquots of the latter re-heat-treated in argon for 1 h at 400, 500 or 700°C (RHT400, RHT500 and RHT700, respectively).

(B) Thermogravimetry using a heating rate of 10 K min⁻¹ and under argon flow of the O-catalyst and AW-catalyst.

(C-D) Ion mass-spectrometry for m:q = 35 (assigned to Cl) and m:q = 44 (assigned to CO_2) that was acquired simultaneously with the thermogravimetry shown in (B).

Modeling the Boehm titration experiment

This section explains how the modeling curve of Fig.8(B) was calculated and demonstrates the equations shown in Fig.8(B); equations that were used to extract from the experimental curve the values for pKa and B_0. The concentration B_0 is defined as the total number of moles of basic groups, originating from the catalyst-surface, per volume of solution. The initial solution (before addition of an aliquot of the original catalyst) was a dilute solution of either H_2SO_4 or NaOH.

The volumetric concentration B_0 is related to the concentration of surface groups per mass of catalyst (M_0, in mol g^{-1}) by the following relation

$$B_0 = M_0 \cdot m/v \qquad\qquad [1]$$

Where m and v are the mass of original catalyst and the volume of initial solution, respectively.

The initial pH (before addition of mass m of catalyst) is pH_i while the final pH, after addition of mass m of catalyst and equilibration, is pH_f.

Analytical solutions were found when the problem was analyzed, on one hand, for low pH_i-values and, on the other hand, for high pH_i-values. The two analytical branches form the whole curve that is shown in Fig.8(B).

<u>Case A: low pH_i-values</u>

The basic groups on the catalyst surface are assumed to bind protons according to the reaction $B + H^+ \leftrightarrow BH^+$.

Accordingly, the initial and final concentrations of reactants and products are

$$B \quad + \quad H^+ \quad \leftrightarrow \quad BH^+$$

Initial state B_0 h   0

Final state $(B_0 - y)$ $(h - y)$ y
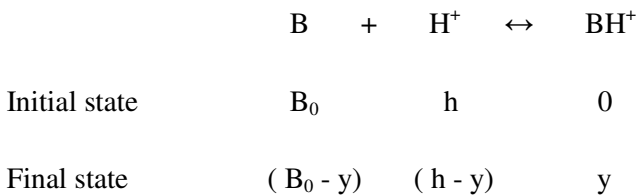
At equilibrium, one has

$$K_a = (B_0 - y) \cdot (h - y)/y \qquad\qquad [2]$$

where K_a is the acidity constant of BH^+, the conjugate acid of the base B.

The final pH value is $pH_f = -\log(h-y)$. The value h is known because the initial pH is known. Therefore, the goal is to calculate y from known values of B_0, h and K_a. Equation [2] is re-written in the form of a second order equation for y:

$$y^2 - y \cdot (h + K_a + B_0) + B_0 \cdot h = 0 \qquad [3]$$
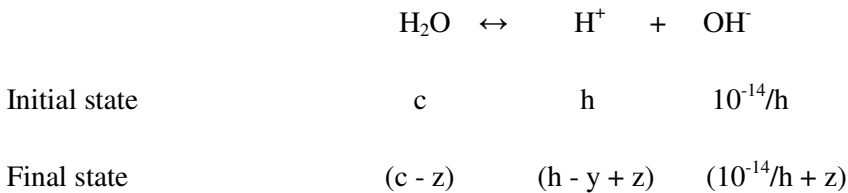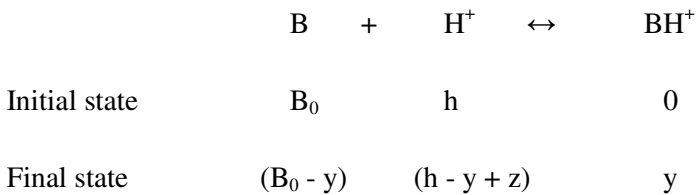
The positive root of this equation is

$$y = [(h + K_a + B_0) - \sqrt{\Delta}]/2 \quad \text{with} \quad \Delta = (h + K_a + B_0)^2 - 4 \cdot B_0 \cdot h \qquad [4]$$

Equation 4 is used to draw the first branch of the calculated curve pH_f vs. pH_i.

Case B: high pH_i-values

At pH_i-values around 7 (5 to 9), a buffering effect induced by water dissociation is not negligible in the calculation of the final pH. Two reactions need to be considered: $B + H^+ \leftrightarrow BH^+$ and $H_2O \leftrightarrow H^+ + OH^-$. Accordingly, the initial and final concentrations of reactants and products are

	B	+	H^+	$\leftrightarrow$	BH^+
Initial state	B_0		h		0
Final state	$(B_0 - y)$		$(h - y + z)$		y

	H_2O	$\leftrightarrow$	H^+	+	OH^-
Initial state	c		h		$10^{-14}/h$
Final state	$(c - z)$		$(h - y + z)$		$(10^{-14}/h + z)$

In the above, the initial concentration of OH^- was directly calculated from the initial concentration of H^+, using the dissociation constant for water, 10^{-14}. The final pH value is $pH_f = -\log(h-y+z)$. Therefore, the goal is to calculate y and z from known values of B_0, h, c and K_a.

Two equations must be verified at equilibrium (final state):

$$K_a = (B_0 - y) \cdot (h-y+z)/y \qquad [5]$$

$$10^{-14} = (h-y+z) \cdot (10^{-14}/h + z) \qquad [6]$$

This is a non-linear system of two equations with two unknowns and can only be solved numerically, in the general case.

However, it simplifies when $y \ll B_0$. This corresponds to a case where a very small fraction of basic groups B become protonated. This assumption will always be valid above a certain value of pH_i, i.e. when the initial concentration of H^+ is far lower than that of basic groups, B_0.

Case B, with $y \ll B_0$:

Equation 5 simplifies to

$$y = B_0 \cdot (h+z)/(K_a+B_0) \tag{7}$$

Then, the unknown y in Eq.6 is replaced by Eq.7, leading after rearrangement to the following second order equation for the unknown z.

$$z^2 + z \cdot (h + 10^{-14}/h) - (10^{-14} \cdot B_0/K_a) = 0 \tag{8}$$

The positive root of this equation is

$$z = [\sqrt{\Delta} - (h + 10^{-14}/h)]/2 \text{ with } \Delta = (h + 10^{-14}/h)^2 + 4 \cdot 10^{-14} \cdot B_0/K_a \tag{9}$$

Equation 9 is used to draw the second branch of the calculated curve pH_f vs.pH_i.

Simple estimation of B_0 and K_a values from an experimental curve pH_f vs. pH_i

At low pH, it is mathematically verified that at equivalence ($h = B_0$), the calculated curve pH_f vs.pH_i shows an inflection point (see Fig.8B, solid line). Thus, the inflection point seen at low pH on an experimental curve of pH_f vs.pH_i can be used to estimate the value of B_0. The value of initial pH for which the inflection point is obtained is

$$pH_{i, \text{ inflection}} = -\log(h) = -\log(B_0) \tag{10}$$

Then, to estimate the K_a-value (or rather, the pK_a value), an analytical expression was found for the plateau of final pH observed at medium values of initial pH (6 to 8).

The existence of this plateau is predicted by calculations only when $K_a \ll B_0$.

<u>Case B, with y << B_0 and K_a << B_0</u>

Then, we have B_0/K_a >> 1, and one can assume that $4 \cdot 10^{-14} \cdot B_0/K_a$ >> $(h + 10^{-14}/h)^2$, and also that $(4 \cdot 10^{-14} \cdot B_0/K_a)^{1/2}$ >> $(h + 10^{-14}/h)$. Accordingly, Eq.9 simplifies to

$$z = [(4 \cdot 10^{-14} \cdot B_0/K_a)^{1/2}] / 2 = 10^{-7} \cdot B_0/K_a \qquad [11]$$

This simplified expression for z is combined with Eq.7 to give the expression of y:

$$y = [h + 10^{-7} \cdot (B_0/K_a)^{1/2}] \cdot B_0 / (K_a + B_0) \qquad [12]$$

Furthermore, due to the assumption K_a << B_0, one can also approximate $B_0/(K_a+B_0)$ in Eq.12 with $1 - K_a/B_0$ (Taylor development of the function $1/(1+x)$ at small x-values). Thus, the expression of y further simplifies to

$$y = [h + 10^{-7} \cdot (B_0/K_a)^{1/2}] \cdot (1- K_a/B_0) \qquad [13]$$

The concentration of protons at equilibrium is $(h - y + z)$. Using Eqs. 11 and 13, one finds

$$h - y + z = K_a \cdot h/B_0 + 10^{-7} \cdot (K_a/B_0)^{1/2} \qquad [14]$$

If a plateau for the final pH is calculated, it necessarily means that the value for the plateau is independent of the initial pH, i.e. independent of h. Thus, the term $K_a \cdot h/B_0$ must be negligible compared to $10^{-7} \cdot (K_a/B_0)^{1/2}$. This is indeed verified because the plateau always appears in calculated curves at neutral or slightly alkaline pH, and also because the plateau is observed only if K_a << B_0 (i.e. K_a/B_0 << $(K_a/B_0)^{1/2}$). Thus, the plateau for the final pH is

$$pH_{f, Plateau} = -\log(h-y+z) = - \log[10^{-7} \cdot (K_a/B_0)^{1/2}] = 7 + 0.5 \log B_0 + 0.5 pK_a \qquad [15]$$

Since the value of B_0 can be estimated from experimental data at the inflection point seen at low initial pH, the experimental plateau of final pH observed near neutral initial pH-values can be used in combination with the above equation to estimate an average pK_a-value of the basic functionalities present on the catalyst.

If no plateau is experimentally observed, it means that the assumption K_a << B_0 is not true. In that case, the pK_a value is best estimated by fitting the whole experimental curve with calculated curves obtained for different values of K_a, until the fit becomes satisfactory.