Facile synthesis of highly active and durable PdM/C (M = Fe, Mn) nanocatalysts for oxygen reduction reaction in alkaline medium

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A°) Description of the method used for the evaluation of ECSA

The electrochemical active surface area (ECSA) is used to compare different catalyst and to normalize the kinetic current. In literature, various methods can be used to determine ECSA of metals: adsorption/desorption of hydrogen (if it exists), stripping of probe molecule (CO, if it is possible), stripping of under potential deposition (UPD) or reduction of oxide.\(^1\) It is well-known that Pd (and in particular PdNPs) has the ability of absorbing hydrogen into its crystal lattice.\(^2\) For avoiding this phenomenon, we did not use the hydrogen adsorption/desorption region method but the reduction peak of palladium oxide (PdO) to determine ECSA. A charge density of 424 μC cm\(^{-2}\) (\(Q_m\)) was associated to the reduction of the formed PdO monolayer.\(^3\) Figure S1 shows the integrated region of interest. The exchange charge (\(Q_{\text{ex}}\)) from Eq. (1) can be assessed by two independent methods either using “integration approach” (e.g. Origin\(^\text{®}\) software) or the old method namely “weighing method or Lavoisier’s approach” from Eq. (2).\(^4\) The “weighing method” uses a tracing paper as reference for weighing on an ultra-sensitive balance. Briefly, it involves cutting a known surface of tracing paper (\(s_0\)) and weighing it. The variables \(a, b, x, y\) and \(v\) used in Eq. (2) are represented in Figure S1. The variable \(m_0\) is the weight of this tracing paper while \(m_1\) is the weight of the shaded curve printed on any paper and modeled (on the tracing paper). Eq. (3) corresponds to the calculation of the active surface area in cm\(^2\).

\[
Q_{\text{ex}} = \frac{1}{v} \int_{E_{\text{onset}}}^{E_{\text{end}}} i(E) dE
\]

(1)

\[
Q_{\text{ex}} = \frac{m_1}{m_0} \times \frac{s_0}{x \times y} \times \frac{a \times b}{v}
\]

(2)

\[
\text{SA(cm}^2) = \frac{Q_{\text{ex}}}{Q_m}
\]

(3)

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**Fig. S1** Illustration of the method used for ECSA evaluation by CV: 5 mV s\(^{-1}\); 0.1 mol L\(^{-1}\) KOH.
B. Fundamentals of Oxygen Reduction Reaction in aqueous medium

B-1. General concepts

The different steps of ORR in aqueous medium (pH = 0-14) can be found in many reviews. The overall reaction for the direct four-electron pathway, which takes place in alkaline medium is described by Eq. (1) and involves the redox couple O$_2$/HO$^-$. 

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightleftharpoons 4\text{HO}^-$$  \hspace{1cm} (4)

The theoretical point in experimental conditions where the ORR, as any electron-driven reaction should start is called the equilibrium potential ($E_{eq}$) that is defined as the potential at zero current. $E_{eq}$ is a thermodynamic parameter and can be numerically calculated from the Nernst equation, by Eq. (5) in alkaline medium. Remember that in this case, the potential is scaled with the Standard Hydrogen Electrode (SHE).

$$E_{O_2/\text{HO}^-}/(\text{V vs. SHE}) = E_{O_2/\text{HO}^-}^0 + \frac{RT}{4F} \ln \left( \frac{C_{O_2}}{C^0} \cdot \frac{\left[H^+\right]}{\left[\text{HO}^-ight]} \right)$$  \hspace{1cm} (5)

C$^0$(= mol L$^{-1}$): reference molar concentration. R(= 8.314 J K$^{-1}$ mol$^{-1}$): gas constant. T(= 273.15+ $\theta$, where $\theta$ is the temperature in °C): temperature in Kelvin. F(= 96 485 C mol$^{-1}$): Faraday’s constant. $C_{O_2}$ (mol L$^{-1}$): oxygen solubility. $E_{O_2/\text{HO}^-}^0$ (= 0.399 V vs. SHE) is the standard equilibrium potential of O$_2$/HO$^-$. 

Note that SHE is a virtual reference electrode and cannot be fabricated experimentally because it involves standard conditions (1 bar, pH = 0). So, during ORR experiments, many reference electrodes are currently used. Depending on the electrolytic medium (which induces the pH value, and chemical species constant change), it is more convenient to convert these values versus the Reversible Hydrogen Electrode (RHE). In the case of SHE, the conversion of the equilibrium potential into RHE is described by Eq. (6) in alkaline medium.

$$E_{eq} = E_{O_2/\text{HO}^-}/(\text{V vs. RHE}) = \left\{ E_{O_2/\text{HO}^-}^0 + \frac{RT}{4F} \ln \left( \frac{C_{O_2}}{C^0} \cdot \frac{\left[H^+\right]}{\left[\text{HO}^-ight]} \right) \right\} - \left\{ E_{H^+/\text{H}_2}^0 + \frac{RT}{4F} \ln \left( \frac{\left[H_2\text{O}^+ight]}{C^0} \right) \right\}$$

$$E_{eq} = E_{O_2/\text{HO}^-}/(\text{V vs. RHE}) = E_{O_2/\text{HO}^-}^0 + \frac{RT}{4F} \ln \left( \frac{C_{O_2}}{C^0} \times \frac{1}{K_e^e} \right)$$  \hspace{1cm} (6)

where $E_{O_2/\text{HO}^-}^0 = 0.399$ V vs. SHE, $E_{H^+/\text{H}_2}^0 = 0.000$ V vs. SHE and Ke = 10$^{-14}$ (in SI unit) at 25 °C.

All the important data involved in the ORR results are gathered in Table 1. It is obvious that any change of the experimental conditions induces a variation of $E_{eq}$. 

3
Table S1. Fundamental basic data of the ORR at 25-50 °C in different supporting electrolytes.

<table>
<thead>
<tr>
<th>Electrolyte solution (25 °C, 1 atm)</th>
<th>$E_{eq}^{[a]}$ (V vs. RHE)</th>
<th>$D_{O_2}^{[b]}$ (cm$^2$ s$^{-1}$)</th>
<th>$\nu^{[b]}$ (cm$^2$ s$^{-1}$)</th>
<th>$C_{O_2}^{[b]}$ (mol cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M H$_2$SO$_4$ (Refs.[8])</td>
<td>1.184</td>
<td>2.01×10$^{-5}$</td>
<td>1.07×10$^{-2}$</td>
<td>1.03×10$^{-6}$</td>
</tr>
<tr>
<td>0.1 M HClO$_4$ (Refs.[8a,8c,9])</td>
<td>1.185</td>
<td>1.93×10$^{-5}$</td>
<td>1.01×10$^{-2}$</td>
<td>1.26×10$^{-6}$</td>
</tr>
<tr>
<td>0.1 M NaOH (Refs.[8c,8d])</td>
<td>1.183</td>
<td>1.90×10$^{-5}$</td>
<td>9.97×10$^{-3}$</td>
<td>8.35×10$^{-7}$</td>
</tr>
<tr>
<td>0.1 M KOH (Refs.[8c,8d])</td>
<td>1.185</td>
<td>1.90×10$^{-5}$</td>
<td>1.00×10$^{-2}$</td>
<td>1.2×10$^{-6}$</td>
</tr>
</tbody>
</table>

$^{[a]}$ Calculated from Nernst-based equations. $^{[b]}$ From the indicated literature references.

B.2. Data analysis through ORR equations

Assuming a planar electrode or a thin film (RDE/RRDE), the use of Koutecky-Levich equation (KL) implicitly requires the two criteria: (i) The existence of an electron transfer process that is the rate determining step $r_{ds}$; (ii) the reaction is of a first-order reaction with respect to the electro-reactive species (O$_2$). The above specific conditions are met in the mixed control regime. Thus, the kinetic current density ($j_k$) and the current density related to mass transport process ($j_{diff}$) give the total current density ($j$) as the sum of reciprocals, Eq. (7). This expression is known as the Koutecky-Levich equation.$^{[8b,8d,10]}$ It should be noticed that all the current densities are normalized with the geometric surface area.

$$
\frac{1}{j} = \frac{1}{j_{diff}} + \frac{1}{j_k} = \frac{1}{j_{diff}} + \frac{1}{j_{film}} + \frac{1}{j_{ads}} + \frac{1}{j_0} \frac{n}{\theta_0 e^{b'}}
$$

$$
\begin{align*}
\text{j}_{app} &= j_0 \frac{0}{\theta_0 e^{b'}} ; \eta = E - E_{eq} ; b' = \frac{RT}{anF} ; j_{diff} = n_{ex} B \Omega^2 \frac{1}{2} \text{ where } B = 0.201 F \nu \frac{1}{7} C_{O_2} D^2 \\
\end{align*}
$$

- $j$: measured ORR current density at the disk (mA cm$^{-2}$),
- $j_{diff}$: diffusion-limiting current density of O$_2$ in the bulk electrolyte (mA cm$^{-2}$),
- $j_{film}$: diffusion-limiting current density of O$_2$ inside the film of the catalytic ink (mA cm$^{-2}$),
- $j_{ads}$: diffusion-limiting current density associated with O$_2$ adsorption at the active site (mA cm$^{-2}$),
- $j_k$: kinetic current density, that is free from the mass transport (mA cm$^{-2}$)
- $j_0$: exchange current density (mA cm$^{-2}$),
- $n_{ex}$: overall exchanged electrons number (total),
- n: number of transferred electrons during the $r_{ds}$ ($n \leq n_{ex}$),
- b': Tafel slope (V),
- $\alpha$: symmetric factor or the charge transfer coefficient (0 < $\alpha$ ≤ 1)
• $\eta = |E - E_{eq}|$, overpotential (V),
• $\theta, \theta_{eq}$: degree of coverage of the catalyst surface (active sites) by oxygen at potential $E$ and at the equilibrium potential $E_{eq}$, respectively,
• $D_{O_2}$: diffusion coefficient of $O_2$ in solution (cm$^2$ s$^{-1}$),
• $C_{O_2}$: the bulk concentration of $O_2$ in the electrolyte (10$^{-3}$ mol cm$^{-3}$),
• $\nu$: kinematic viscosity of the electrolyte (cm$^2$ s$^{-1}$),
• $F$: Faraday’s constant ($F = 96485$ C mol$^{-1}$),
• $\Omega$: RRDE speed (rpm).

The electrochemical and hydrodynamic properties of RDE/RRDE are correlated with the KL equation that can be expressed by Eq. (10). It becomes thereafter Eq. (9) when $\Omega \to \infty$. This relation enables getting experimentally the kinetic current density ($j_k$).

\[
\frac{1}{j} = \frac{1}{j_{ex} B \Omega^{\frac{3}{2}}} + \frac{1}{j_{lim}} + \frac{1}{j_{ads}} + \frac{1}{j_{app}} \quad \Rightarrow \quad \lim_{\Omega \to \infty} \left( \frac{1}{j} \right) = \frac{1}{j_{lim}} + \frac{1}{j_{ads}} + \frac{1}{j_{app}} \quad (8)
\]

\[
\frac{1}{j_k} = \frac{1}{j_{lim}} + \frac{1}{j_{ads}} + \frac{1}{j_{app}} \quad (9)
\]

\[
\frac{1}{j} = \frac{1}{j_{ex} B \Omega^{\frac{3}{2}}} + \frac{1}{j_{lim}} + \frac{1}{j_{ads}} + \frac{1}{j_{app}} \quad \Rightarrow \quad j^{-1} = \left( j_{ex} B \right)^{-1} \Omega^{\frac{-3}{2}} + j_k^{-1} \quad (10)
\]

From Eq. (10), the curve $j^{-1}$ versus $\Omega^{\frac{1}{2}}$ that is known as “Koutecký–Levich plot” is a straight line characterized by a KL slope $\alpha_{KL} = (j_{ex} B)^{-1}$ and a KL intercept $\beta_{KL} = j_k^{-1}$. The slope of the straight line enables extracting the total number of exchanged electrons $n_{ex}$ and the intercept at the origin ($\Omega \to \infty$) gives the inverse of the kinetic current $j_k$. The determined $j_k$ from the intercepts is expressed in mA per cm$^2$ of disc (sample), referred as “absolute activity”.$^{[11]}$ Then, and as recommended,$^{[11]}$ $j_k$ must be normalized as:

(i) the “area-specific activity” $A_s$ (mA per cm$^2$ metal: mA cm$^{-2}$ metal or mA cm$^{-2}$) by dividing the absolute activity by the surface-area enhancement factor,

(ii) the “mass activity” $A_m$ (mA per µg of metal: mA µg$^{-1}$ metal) by dividing the absolute activity by the metal loading.

The surface-area enhancement factor (also referred as the electrochemical surface roughness or electrode roughness) is the ECSA of the catalyst divided by the planar area of the sample (cm$^2$ metal per planar cm$^2$).

In the KL equation, especially in Eq. (9), it is impossible to separate contributions from $j_{lim}$ and $j_{ads}$ since they do not depend on the rotation rate. They are gathered as $j_L$ (Eq. (11)) that is
defined as a *limiting current density resulting from a mixed-control by the diffusion of O₂ inside the film of the catalytic ink and by the adsorption of O₂ at the active sites*. The expression of \( j_k \) becomes thereafter Eq. (13), a relationship between \( j_L \) and \( j_k^{\text{app}} \).

\[
\frac{1}{j_L} = \frac{1}{j_{L,\text{film}}} + \frac{1}{j_{L,\text{ads}}} \tag{11}
\]

\[
\frac{1}{j_k} = \frac{1}{j_{k,0}} + \frac{1}{j_{k,0}^{\eta} e^{b/\eta}} \tag{12}
\]

\[
\frac{1}{j_k} = \frac{1}{j_{k,0}} + \frac{1}{j_{k,0}^{\eta} e^{b/\eta}} = \frac{1}{j_{k,0}} + \frac{1}{j_{k,0}^{\eta} e^{b/\eta}} \Rightarrow \lim_{\eta \to \infty} \left( \frac{1}{j_k} \right) = \frac{1}{j_{k,0}} \tag{13}
\]

Eq. (12) becomes thereafter Eq. (13) when \( \eta \to \infty \), meaning \( E \ll E_{\text{eq}} \) because \( E < E_{\text{eq}} \) for reduction reactions like ORR. Therefore, \( j_k \) is determined experimentally after extrapolating the reported \( j_k^{-1} \) values as a function of the potential \( E \).

Supposing that the coverage of the catalyst surface (active sites) by O₂ at potential \( E \) and at the equilibrium potential \( E_{\text{eq}} \) is quite the same (\( \theta \approx \theta_{\text{eq}} \)), Eq. (12) becomes relationship Eq. (14). If there is no competitive reaction involving the catalyst surface in the whole potentials range of interest, the experiments will meet the hypothesis by bubbling continuously O₂.

\[
\frac{1}{j_k} = \frac{1}{j_{k,0}} + \frac{1}{j_{k,0}^{\eta} e^{b/\eta}} = \frac{1}{j_{k,0}} + \frac{1}{j_{k,0}^{\eta} e^{b/\eta}} = \frac{1}{j_{k,0}} + \frac{1}{j_{k,0}^{\eta} e^{b/\eta}} \Rightarrow \frac{E - E_{\text{eq}}}{b} = \ln\left(\frac{j_k}{j_{k,0}} \times \frac{j_{k,0}}{j_L - j_k}\right) \Rightarrow \frac{E - E_{\text{eq}}}{b} = -\frac{\ln\left(\frac{j_k}{j_{k,0}}\right)}{\ln\left(\frac{j_L}{j_L - j_k}\right)} - \left[\log\left(\frac{j_k}{j_{k,0}}\right)\right] = \log\left(\frac{j_k}{j_{k,0}}\right) \tag{15}
\]

\[
\alpha_{\text{Tafel}} = \frac{\partial \eta}{\partial \log\left(\frac{j_k}{j_L - j_k}\right)} \Rightarrow b = -\alpha_{\text{Tafel}} = b \times \ln(10) \approx \frac{2.3RT}{\alpha nF} \tag{16}
\]

\[
\beta_{\text{Tafel}} = -\log\left(\frac{j_k}{j_{k,0}}\right) \Rightarrow j_{0} = j_{L,0} \times 10^{-\beta_{\text{Tafel}}/b} \tag{17}
\]

Plotting either \( \eta \) or \( (E - E_{\text{eq}}) \) versus \( \log\left(\frac{j_k}{j_L - j_k}\right) \) is known as “Tafel plot” (Eq. (15)) and is a straight line characterized by \( \alpha_{\text{Tafel}} = \frac{\partial (E - E_{\text{eq}})}{\partial \log\left(\frac{j_k}{j_L - j_k}\right)} = -b \) that enables getting the Tafel slope (expressed
in mV dec\(^{-1}\)) via Eq. (16) and the intercept \(\beta_{\text{act}} = -b \log \left( \frac{j_0}{j_L} \right) \) from which the exchange current density \(j_0\) is determined through Eq. (17).

The major benefit of RRDE equipment for ORR is the determination of the reaction intermediate. A RRDE apparatus enables determining the reaction product formation efficiency at the disk that is typically \(\text{H}_2\text{O}\) (acid medium) or \(\text{HO}^-\) (alkaline medium), in direct relationship with the amount of the reaction intermediate (\(\text{H}_2\text{O}_2\) or \(\text{HO}_2^-\)). The method was firstly developed by Jakobs et al.\cite{12} in 1985 and then revised by Vork and Barendrecht in 1990.\cite{13} During the ORR, \(\text{O}_2\) is reduced at the disk (current: \(I_D < 0\)) and the intermediate \(\text{H}_2\text{O}_2\) or \(\text{HO}_2^-\) is radially swept outward away from the disk and toward the ring where it is oxidized (current: \(I_R > 0\)). The set relationship is given by Eq. (18).\cite{13} It is highly important to note that even if \(N\) is provided in percentage, e.g., 20.5\% herein, it is used in fraction meaning \(N = 0.205\). The \(\text{O}_2\) reduction to \(\text{H}_2\text{O}\) involves 4\(e^-\) and only 2\(e^-\) when the reaction process leads to \(\text{H}_2\text{O}_2\) (or \(\text{HO}_2^-\)). Thus, when both \(\text{H}_2\text{O}\) and \(\text{H}_2\text{O}_2\) (or \(\text{HO}_2^-\)) are produced, \(n_{\text{ex}}\) is easily accessed through Eq. (19).\cite{12,13}

\[
\begin{align*}
p(\text{H}_2\text{O}) &= 1 - p(\text{H}_2\text{O}_2) = \frac{N_{\text{D}} I_R + I_{\text{R}}}{N_{\text{D}} I_R - I_{\text{R}}} = \frac{1 - \frac{I_R}{N I_{\text{D}}}}{1 + \frac{I_R}{N I_{\text{D}}}} \quad (18) \\
n_{\text{ex}} &= n_{(\text{O}_2 \rightarrow \text{H}_2\text{O})} + n_{(\text{O}_2 \rightarrow \text{H}_2\text{O}_2)} = 4p(\text{H}_2\text{O}) + 2p(\text{H}_2\text{O}_2) = 2\left[p(\text{H}_2\text{O}) + 1\right] - \frac{4N I_{\text{D}}}{I_R + N I_{\text{D}}} = \frac{4}{1 + \frac{I_R}{N I_{\text{D}}}} \leq 4 \quad (19)
\end{align*}
\]

The complete ORR study requires a RRDE that has the advantage of analyzing the short-life intermediate in a steady-state measurement.\cite{10b} To this end, one needs a four-electrode potentiostat, also referred as a double/bi-potentiostat that enables controlling the potential of the disc and the ring with respect to the reference electrode independently and measuring the current through each of them separately. Typically, the potential of the ring is hold at a fixed value (\(E_{\text{R}}\)) and that of the disk is varied to analyze the products formed at it surface by studying the ring current (\(I_{\text{R}}\)) as a function of the disk potential (\(E_{\text{D}}\)), or vice versa. RRDE must be calibrated by determining its collection efficiency \(N\), which is defined as the fraction of a species formed at the disc that arrives at the ring and reacts there \cite{10b} It is specific to the RRDE geometry and does not depend on the studied redox reaction. The easy and elegant way to evaluate experimentally \(N\) consists of considering a simple reduction reaction, for example, \(\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}\) from \([\text{Fe(III)(CN)}_6]^{3-} + e^- \rightarrow [\text{Fe(II)(CN)}_6]^{4-}\). It is calculated from Eq. (20) only valid for currents, not the current densities! \(E_{\text{R}}\) must be higher than the potential where the involved intermediate is oxidized (e.g. 0.77 V vs. RHE for \(\text{Fe}^{3+}/\text{Fe}^{2+}\) system). For the ORR, \(E_{\text{R}} \sim 1.1-1.3\) V vs. RHE.

\[
N = \frac{I_{\text{R}}}{I_{\text{D}}} = \frac{I_{\text{R}}}{|I_{\text{D}}|} \leq 1 \quad (20)
\]
**C. Additional Tables and Figures**

Table S2. Comparative performances from ORR-RRDE experiments (0.1 M KOH) on the as-synthesized PdM/C (M = Fe, Mn) nanocatalysts during APCT. \( E_{1/2} \) was graphically determined at 1600 rpm (E at \( i = I_{D/2} \)). Note: “BAE” refers to Bromide Anion Exchange and “Pol” refers to Polyol.

<table>
<thead>
<tr>
<th>Electrode material at ( p ) cycle (( k = 1000 ))</th>
<th>( E_{eq(exp)} )</th>
<th>( E_{1/2} ) at 1600 rpm</th>
<th>Tafel slope (mV dec(^{-1}))</th>
<th>( j_0 ) (( \times 10^{-3} ) mA cm(^{-2} ))</th>
<th>( j_k )</th>
<th>( n_{ex} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>p</strong></td>
<td><strong>Catalyst</strong></td>
<td>V vs. RHE</td>
<td>( \eta )</td>
<td>( \eta )</td>
<td>( \eta )</td>
<td>( \eta )</td>
</tr>
<tr>
<td><strong>20</strong></td>
<td>Pd/C-BAE</td>
<td>1.052</td>
<td>0.86</td>
<td>65</td>
<td>125</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>PdFe/C-BAE</td>
<td>1.023</td>
<td>0.85</td>
<td>85</td>
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<tr>
<td></td>
<td>PdFe/C-Pol</td>
<td>1.002</td>
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<td>174</td>
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</tr>
<tr>
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<td>PdMn/C-BAE</td>
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<td>0.87</td>
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<td>165</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>PdMn/C-Pol</td>
<td>1.056</td>
<td>0.86</td>
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<td>159</td>
<td>0.64</td>
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<tr>
<td><strong>5k</strong></td>
<td>Pd/C-BAE</td>
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<td>0.85</td>
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<td></td>
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<td>0.85</td>
<td>79</td>
<td>158</td>
<td>0.34</td>
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<td><strong>10k</strong></td>
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<tr>
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<td>0.83</td>
<td>83</td>
<td>159</td>
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<tr>
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<td>PdFe/C-Pol</td>
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<td>167</td>
<td>0.01</td>
</tr>
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<td>76</td>
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<tr>
<td><strong>15k</strong></td>
<td>Pd/C-BAE</td>
<td>1.048</td>
<td>0.82</td>
<td>66</td>
<td>131</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
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<td>0.81</td>
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<td>134</td>
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Fig. S2 Typical ORR polarization curves recorded at 5 mV s\(^{-1}\) scan rate in O\(_2\)-saturated 0.1 mol L\(^{-1}\) KOH solution at the ring (top) and disc (bottom) for different speeds of RRDE: (a)-(e) PdMn/C-BAE (From 20\(^{th}\) to 20,000\(^{th}\) APCT) and (f) PdFe/C-BAE (20,000\(^{th}\) ACPT). For all panels, current densities are obtained with the geometry surface area of the ring (0.110 cm\(^2\)) and disc (0.196 cm\(^2\)).
Fig. S3 Typical ORR polarization curves recorded at 5 mV s\(^{-1}\) scan rate in \(\text{O}_2\)-saturated 0.1 mol L\(^{-1}\) KOH solution at the ring (top) and disc (bottom) for different speeds of RRDE: (a)-(e) PdMn/C-Pol (From 20\(^{th}\) to 20,000\(^{th}\) APCT) and (f) PdFe/C-Pol (20,000\(^{th}\) ACPT). For all panels, current densities are obtained with the geometry surface area of the ring (0.110 cm\(^2\)) and disc (0.196 cm\(^2\)).
Fig. S4 Typical plots obtained from the ORR polarization curves recorded at 5 mV s$^{-1}$ scan rate: Example for PdMn/C-BAE_20 (after 20$^{th}$ CV) electrode material. (a) Koutecky–Levich plots from. (b) "$j_k^{-1}$ versus $E$" plot for the determination of the limiting current density $j_L$. (c) Tafel plots: The limiting current density $j_L$ was determined from the "$j_k^{-1}$ versus potential" plots and a value of $E_{eq} = 1.185$ V vs. RHE in 0.1 mol L$^{-1}$ KOH was considered. (d) HO$_2^-$ (H$_2$O$_2$ in acid media) percentage from the incomplete ORR (left Y-axis) and the number of electrons exchanged $n_{ex}$ (right Y-axis) determined from ORR polarization curves in O$_2$-saturated 0.1 mol L$^{-1}$ KOH at 5 mV s$^{-1}$ scan rate and RRDE speed of 1600 rpm.

Note: For all panels, the current densities are obtained with the geometry surface area of the ring (0.11 cm$^2$) and disc (0.196 cm$^2$).
Fig. S5 Kinetic parameters obtained from ORR polarization curves recorded at 5 mV s\(^{-1}\) in 0.1 mol L\(^{-1}\) KOH during APCT. (a) Kinetic current density \(j_k\), determined from Koutecky–Levich plots at 0.85 V vs. RHE and referred as “Mass activity” (mA per mg of Pd). (b) Exchange current density \(j_0\) (normalized with geometry surface area of the disc: 0.196 cm\(^2\)) and determined at low overpotential (high potentials or low currents) where the Tafel slope is 60-85 mV dec\(^{-1}\) (Temkin adsorption isotherms of oxygenated species).
**Fig. S6** Surface atomic composition as-determined from XPS.
References


