Supporting Information

Operando X-Ray Absorption Spectroscopy of Pd/ γ-NiOOH 2nm cubes Hydrogen Oxidation Catalyst in Alkaline Membrane Fuel Cell

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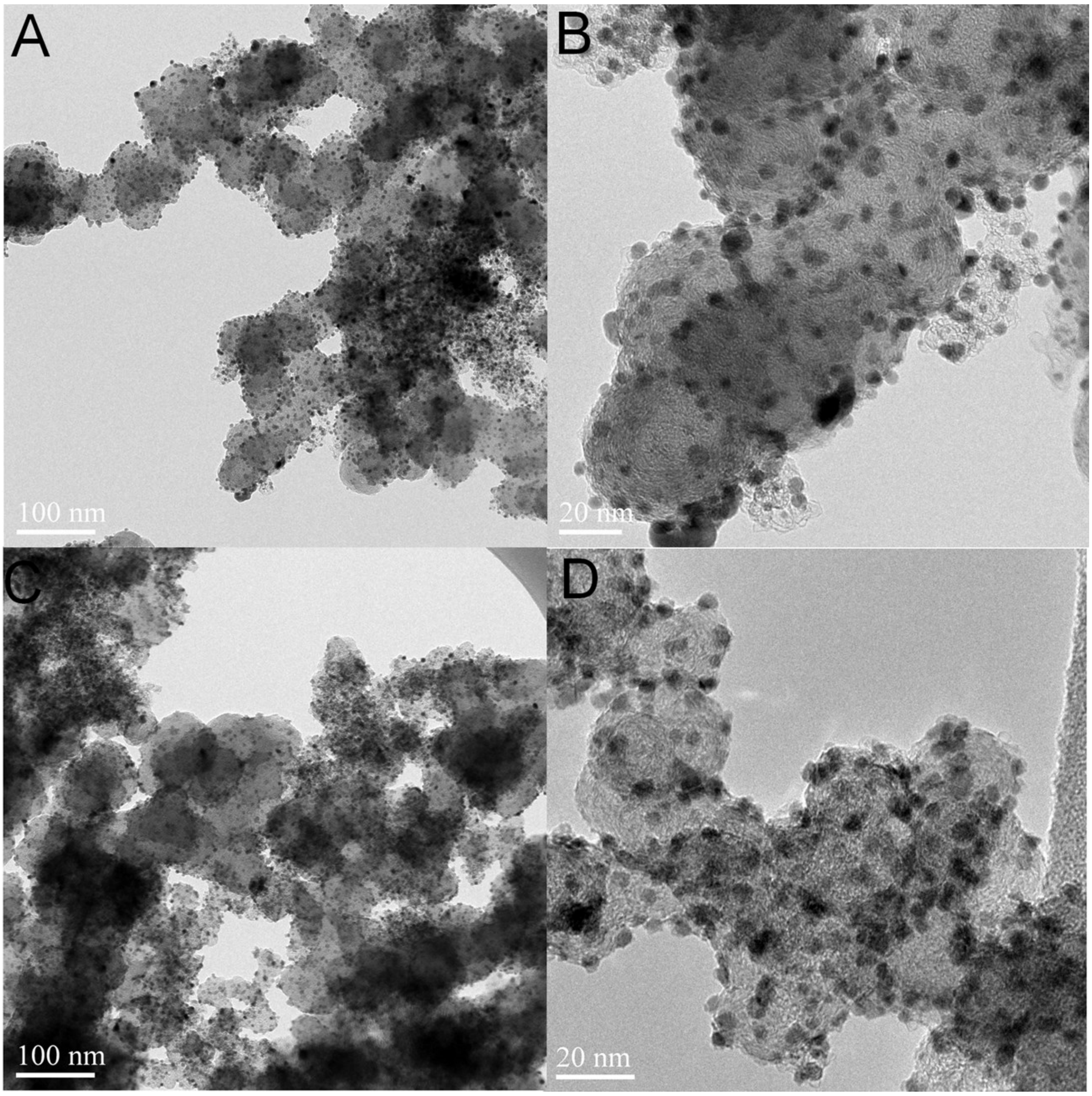


Fig. S1: TEM of the pristine C/Pd sample (A-B) and C/Pd/NiOOH sample (C-D)

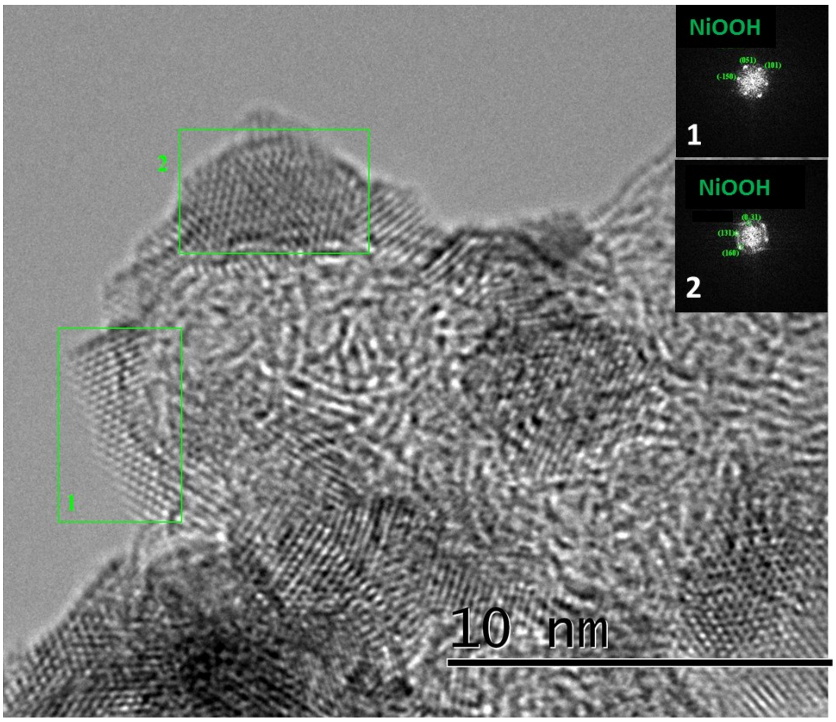


Fig. S2: HRTEM image of Pd/γ-NiOOH with corresponding FFT (insets).

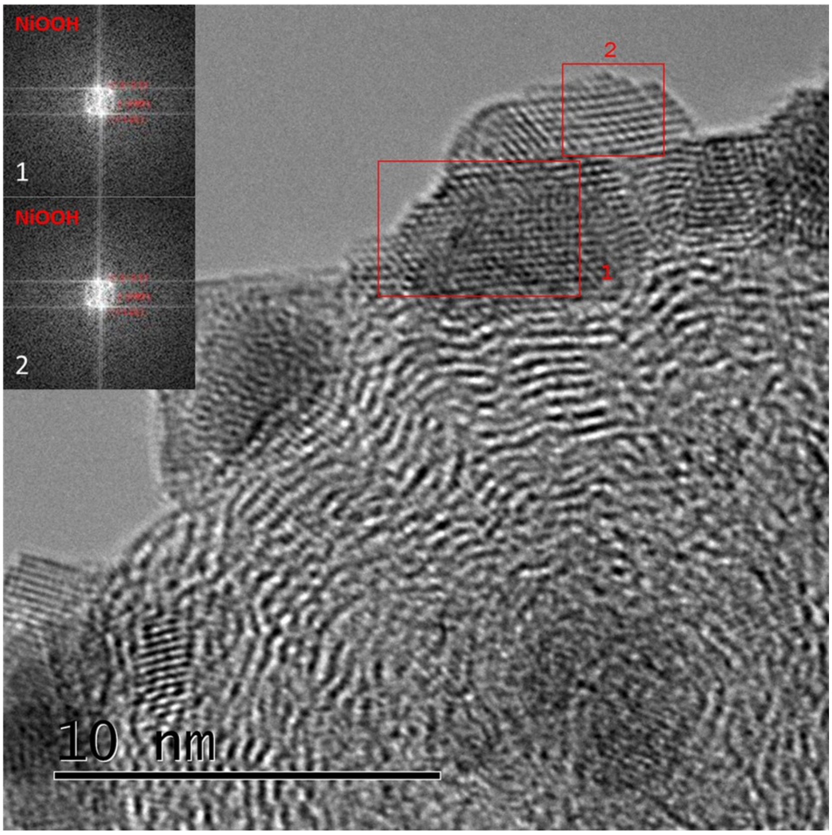
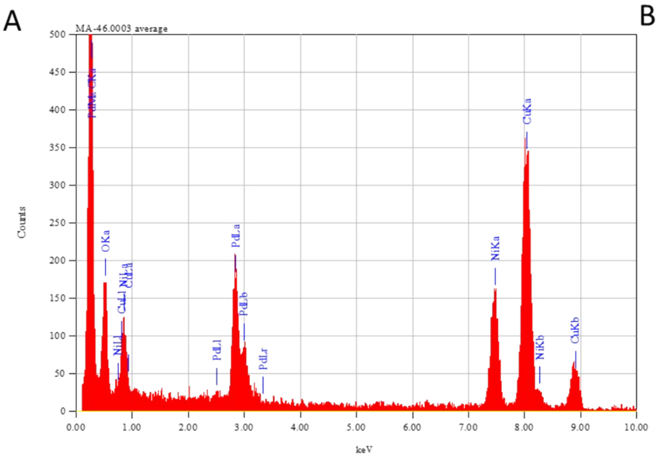


Fig. S3: HRTEM image of Pd/γ-NiOOH with corresponding FFT (insets).



Element	(keV)	Mass%	Counts	Error%	Atom%
O K	0.525	13.70	1036.12	0.03	44.90
Ni K	7.471	31.39	2416.59	0.04	28.04
Pd L*	2.838	54.91	1971.28	0.04	27.06
Total		100.00			100.00

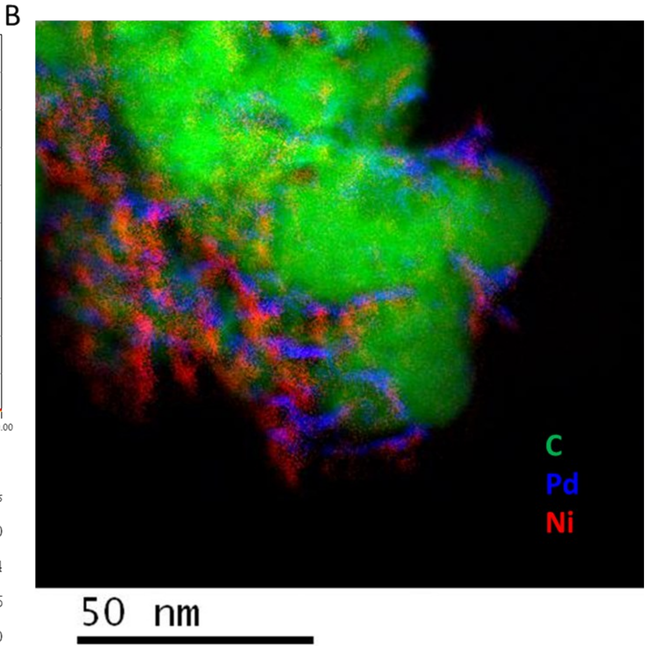


Fig. S4: (a) Energy Dispersive X-ray spectroscopy with the corresponding table of weight and atomic ratios. (b) HAADF-STEM elemental mapping showing the carbon (green), palladium (blue) and nickel (red) distribution (note that a slight drift occurred during the acquisition)

Extraction of the specific activity, mass activity, and exchange current density

The kinetic currents for HOR in alkaline media at 0.01 V vs. RHE were calculated based on the Koutecky–Levich equation[1].

$$I_k = I * I_d/(I_d - I)$$

where I is the measured current (from RDE), and Id indicates the diffusion limited current.

The kinetic currents for HOR in alkaline media at 0.01 V vs. RHE were then normalized to the mass of metals to obtain the mass activity.

$$I_m = I_k/M_m$$

The electrochemical surface area of catalysts (ECSA), was determined from the cathodic peak at 0.65 V/RHE, which is related to the reduction of oxygen species on Pd [2]

The kinetic currents for HOR in alkaline media at 0.01 V vs. RHE were then normalized to the electrochemical surface area to obtain the specific activity.

$$I_{k,s} = I_k/ECSA$$

The exchange current density (i_0) was calculated from the Tafel plots extracted from the plot of Nernstian overpotential (η_d) vs. kinetic current (i_k).

Table S1: Comparison between the Pd-based anode materials for AEMFCs

<table>
<tr><th>Catalyst</th><th>Exchange current density i_0 [mA/cm^2_{PGM}]</th><th>ECSA [m^2/gPGM]</th><th>Mass activity i_m [A/g $_{PGM}$] @0.01V</th><th>Mass activity i_m [A/g $_{PGM}$] @0.1V</th><th>I_s [mA/cm^2_{PGM}] @0.01V</th><th>J @ 0.8V in AEMFC [A/mgPGM]</th><th>Reference</th></tr>
<tr><td>Pd/γ-NiOOH/C</td><td>0.2</td><td>98</td><td>48</td><td>760</td><td>0.05</td><td>0.75</td><td>This study</td></tr>
<tr><td>$Ir_3Pd_1Ru_6/C$</td><td>0.6</td><td>110</td><td>340</td><td>2890</td><td>0.28</td><td>2</td><td>9, 31</td></tr>
<tr><td>Pd/C</td><td>0.025-0.05</td><td>122</td><td>8</td><td>269[3]</td><td>0.006</td><td>0.052</td><td>9, This study</td></tr>
<tr><td>NiPd/C</td><td colspan="5">calculation of exchange current density is very challenging since the specific surface for each metal (Ni and Pd species) is difficult to determine for such a nanocomposite</td><td>0.33</td><td>20</td></tr>
<tr><td>$Pd/C\text{-}CeO_2$</td><td rowspan="2">0.05-0.1</td><td rowspan="2">43</td><td rowspan="2">9-18</td><td rowspan="2">1100[a]</td><td rowspan="2">0.02-0.04[b]</td><td rowspan="2">0.5</td><td>26</td></tr>
<tr><td>$Pd/C\text{-}CeO_2$</td><td>27</td></tr>
</table>

[a] calculated based on Tafel slope (66 mV/dec)

[b] calculated from Butler-Volmer equation for low η

References

[1] W. Sheng, H.A. Gasteiger, Y. Shao-Horn, Hydrogen Oxidation and Evolution Reaction Kinetics on

Platinum: Acid vs Alkaline Electrolytes, Journal of The Electrochemical Society. 157 (2010) B1529. https://doi.org/10.1149/1.3483106.

[2] M. Lukaszewski, M. Soszko, A. Czerwiński, Electrochemical methods of real surface area determination of noble metal electrodes - an overview, International Journal of Electrochemical Science. 11 (2016) 4442–4469. https://doi.org/10.20964/2016.06.71.

[3] E.S. Davydova, S. Mukerjee, F. Jaouen, D.R. Dekel, Electrocatalysts for Hydrogen Oxidation Reaction in Alkaline Electrolytes, ACS Catalysis. 8 (2018) 6665–6690. https://doi.org/10.1021/acscatal.8b00689.