Supplementary Information

Improved Hydrogen Oxidation Reaction Activity and Stability of Buried Metal-Oxide Electrocatalyst Interfaces

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Figure S1. Schematic of the SiRDE assembly.

Region	C1s /	O1s /	Pt4f/	Pd3d /	Ce3d /	Ce atomic	Si2s /	N1s /
Sample	at.%	at.%	at.%	at.%	at.%	ratio / %	at.%	at.%
Pt	49.11	13.76	33.67	0	0.00	0.00	0.53	2.93
Pt-Ce ₄	37.33	11.04	48.53	0	0.30	0.62	0.00	2.79
Pt-Ce ₈	38.97	25.44	30.05	0	0.81	2.63	3.46	1.28
Pt-Ce ₁₂	63.32	14.53	18.41	0	2.19	10.64	0.64	0.91
Pt-Ce ₁₆	47.42	17.67	28.57	0	3.87	11.92	1.56	0.91
Pt-Ce ₂₀	56.57	13.07	25.59	0	3.46	11.92	0.14	1.17
Pd	17.35	59.74	0	20.37	0.00	0.00	0.34	1.60
Pd-Ce ₄	26.94	53.33	0	16.26	0.64	3.80	0.64	1.95
Pd-Ce ₈	33.91	48.84	0	10.80	1.63	13.09	2.71	2.09
Pd-Ce ₁₂	34.71	47.57	0	12.74	3.11	19.63	0.07	1.79
Pd-Ce ₁₆	38.21	46.42	0	9.42	2.91	23.59	1.54	1.50
Pd-Ce ₂₀	41.56	43.10	0	10.68	3.50	24.69	0.00	1.16

Table S1. Quantitative XPS analysis of all samples from survey scans.



Figure S2. Direct comparison of the impact of increasing Ce coverage on the underlying PGM component, which is negligible. Data shown here is background-subtracted and normalized to the most intense peak.

Supplementary XPS Discussion

The Pd3d regions of all samples could be interpreted as if Pd is slightly oxidized, possibly due to the interaction with Ce. This can be concluded, based on Pd3d peak fitting approaches commonly used in electrocatalysis literature. Here, a metallic (Pd⁰3d_{5/2}, 335.2 ± 0.2 eV) and two oxide components (Pd^{II}3d_{5/2}, 336.4 ± 0.2 eV; Pd^{IV}_{5/2}, 338 ± 0.2 eV) are often assigned as symmetric Gauss-Lorentzian curves according to existing literature data. ¹⁻⁷ The spin-orbit component ($\Delta BE = 5.26 \text{ eV}$) with 1/3rd intensity is mirrored with an identical full width half maximum (FWHM) for each of the three components. We want to stress, however, that with a single asymmetric peak component for Pd⁰, which might be a more physically meaningful way of fitting metallic Pt and Pd peaks⁸⁻¹⁰, there are no oxide components necessary to fit the experimental data. The comparison of these fitting approaches is shown in Figure 1D in the main text, where an asymmetric fit was applied to the Pd 3d_{5/2} and a symmetric one to the Pd 3d_{3/2}. Regardless of the fitting shape, we observe no significant impact of CeO_x coverage on the oxidation state of Pd as presented simply through the direct comparison of all spectra shown in Figure S2. Here, no significant changes in both the Pd 3d and Pt 4f regions are observed with increasing CeO_x coverage.

Using the Hill equation (Eq. S1) as a reliable estimation for thin oxide films¹¹, we calculate the film thickness (*t*) from the peak intensities of the film (I_0) and the substrate (I_s) normalized by their respective relative sensitivity factors (S₀, S_s). The photoelectron escape angle (Θ), normal to the film surface at which the spectra were gathered was 85 °.

$$t = -\lambda \cos \theta \ln \left(\frac{I_0 / S_0}{I_s / S_s} \right)$$
 Eq. S1

Here, λ is the effective attenuation length of an electron in the specific media, which was calculated from crystallographic data using Eq. S2.^{12, 13}

$$\lambda = 0.316a^{1.5} \left[\frac{E}{Z^{0.45} \left(\ln \left\{ \frac{E}{27} \right\} + 3 \right)} + 4 \right]$$
 Eq. S2

The effective attenuation length λ was calculated from CeO₂ unit cell parameters *a*, its atomic number *Z*, and the kinetic energy of the passing electron *E*.

Table S2. Resistance through the conductive layer acquired by four-point probe resistivity measurements. The CeOx layer thickness in the range of nm does not impact the conductivity significantly. Differences between Pt and Pd films can be related to slight variations of Ti adhesion layer thickness or PGM thickness during preparation.

Sample	Resistance / Ω
Pt	0.62
Pt-Ce ₄	0.49
Pt-Ce ₈	0.58
Pt-Ce ₁₂	0.49
Pt-Ce ₁₆	0.50
Pt-Ce ₂₀	0.41
Pd	0.32
Pd-Ce ₄	0.22
Pd-Ce ₈	0.22
Pd-Ce ₁₂	0.29
Pd-Ce ₁₆	0.32
Pd-Ce ₂₀	0.23



Figure S3. Film thickness obtained from spectroscopic ellipsometry.



Figure S4. Exemplary AFM data of blank Pt and Pt_{12} through which the arithmetic mean deviation (R_a) was calculated.



Figure S5. The arithmetic mean deviations of all samples, calculated from AFM pictures similar to Figure S4.

Sample	$E_{1/2} \ / \ mV$	j_0 / mA cm ⁻²
Pt	33	1.27
Pt-Ce ₄	28	1.27
Pt-Ce ₈	36	1.41
Pt-Ce ₁₂	57	0.37
Pt-Ce ₁₆	27	0.34
Pt-Ce ₂₀	99	0.15
Pd	435	0.07
Pd-Ce ₄	239	0.25
Pd-Ce ₈	202	0.36
Pd-Ce ₁₂	148	0.69
Pd-Ce ₁₆	125	0.80
Pd-Ce ₂₀	118	1.05

Table S3. Activity descriptors from LSVs similar to Figures 3A and B in the main Text.



Figure S6. LSV on the SiRDE at 1600 rpm in O_2 for Pt (blue) and Pd (green). The lighter traces represent thicker CeO_x coverages. The reverse scan from 0 to 1.2 V_{RHE} is partially depicted.

Sample	E _{on} , anodic /	E _{on} , cathodic /	Anodic dissolved M /	Cathodic dissolved M /
	V_{RHE}	V_{RHE}	$ng cm^{-2}$	$ng cm^{-2}$
Pt	1.01	1	0.17	0.9
Pt-Ce ₄	1.03	0.92	0.11	0.6
Pt-Ce ₈	1.15	0.75	0.04	0.2
Pt-Ce ₁₂	1.21	0.78	0.05	0.2
Pt-Ce ₁₆	1.21	0.7	0.03	0.1
Pt-Ce ₂₀	1.27	0.68	0.03	0.1
Pd	0.99	1.24	14.2	8.6
Pd-Ce ₄	0.98	1.24	12.5	9
Pd-Ce ₈	1.11	1.14	2.2	3.3
Pd-Ce ₁₂	1.1	1.19	2.5	3.7
Pd-Ce ₁₆	1.15	1.16	1.5	2.6
Pd-Ce ₂₀	1.27	1	1	1.4

Table S4. Summarized stability descriptors of each sample obtained from the stability measurements in Figures 3C and D.



Figure S7. The dissolution rate of Ce measured on the Pd-Ce₂₀ sample from Figure 3D in the main text.



Figure S8. Partial CV of Pd_N samples at 200 mV s⁻¹ in Ar purged 0.05 M NaOH. The arrows indicate the lowered and shifted redox features of Pd.

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