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Supporting Information

X-ray Absorption Spectroscopy Investigation of Platinum–Gadolinium Thin Films with Different Stoichiometry for the Oxygen Reduction Reaction

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The X-ray absorption (XAS) measurements were carried out at Stanford Synchrotron Radiation Lightsource (SSRL). The spectra were obtained at the Pt L_3 edge (11,564 eV) in the energy range from 11,334 to 12,464 eV, corresponding to an extended X-ray adsorption fine structure (EXAFS) range up to a photoelectron wavenumber of ~15.4 $Å^{-1}$ and at the Gd L_3 edge (7,243 eV) in the energy range from 7,125 to 7,683 eV, corresponding to an EXAFS range up to a photoelectron wavenumber of ~10.7 $Å^{-1}$ [1]. All EXAFS fitting was done in *R*-space using a k^2-weighting in a *k*-range between ~2 and ~11 $Å^{-1}$, and an *R*-range from ~1.4 to ~3.4 Å.

Scattering paths for fitting were calculated using FEFF8, and paths were generated using standard Pt face centered cubic (FCC), Pt_5Gd (Cu_5Ca structure), and Gd_2O_3 (Mn_2O_3 structure) structures. It should be noted that any Gd coordination with oxygen (or carbon) may originate from the interface between the Pt_xGd thin film and the glassy carbon substrate. For the specific EXAFS fitting, please see the data below.

Table S1. EXAFS data of clean Pt foil taken at 2°, this measurement was used to identify relaxed Pt-Pt distance.

Pt L_3 edge of Pt foil							
Variable	**Value**	**Error**	**Atom**	k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-		3	16	1.75	4.80
e_0	9.00	0.39					
R_1	2.76	0.002	Pt	χ^2	Red(χ^2)	*R*-factor	
N_1	12.71	0.26		9442.0	530.8	0.007	
σ_1	0.005	-					
R_2	3.91	0.007	Pt				
N_2	5.92	0.81					
σ_2	0.007	-					
R_3	4.81	0.006	Pt				
N_3	22.98	2.25					
σ_3	0.008	-					

Table S2. EXAFS data of as-prepared Pt_5Gd (10 nm) sample taken at 2°.

Pt L_3 edge of Pt_5Gd (10 nm) not subjected to electrochemical cycling							
Variable	**Value**	**Error**	**Atom**	k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-		3	14	1.8	3.9
e_0	7.30	0.39					
R_1	2.69	0.003	Pt	χ^2	Red(χ^2)	*R*-factor	
N_1	5.90	0.23		80.5	10.7	0.002	
σ_1	0.008	-					
R_2	2.82	0.015	Pt (Gd)				
N_2	3.18	0.32					
σ_2	0.014	-					
R_3	3.89	0.017	Pt/Gd				
N_3	1.41	0.39					
σ_3	0.01	-					
Gd L_3 edge of Pt_5Gd (10 nm) not subjected to electrochemical cycling							
Variable	**Value**	**Error**	**Atom**	k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-		3	10	1.4	3.1
e_0	11.37	1.67					
R_1	2.39	0.018	O	χ^2	Red(χ^2)	*R*-factor	
N_1	4.10	0.28		272.3	110.4	0.010	
σ_1	0.010	-					
R_2	3.029	0.02	Pt				
N_2	1.46	0.44					
σ_2	0.006						

Table S3. EXAFS data of Pt_5Gd (10 nm) sample after electrochemical cycling taken at 2°.

Pt L_3 edge of Pt_5Gd (10 nm) subjected to electrochemical cycling							
Variable	**Value**	**Error**	**Atom**	k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-		3	14	1.8	4.0
e_0	7.45	0.33					
R_1	2.73	0.002	Pt	χ^2	Red(χ^2)	*R*-factor	
N_1	7.45	0.33		308.9	30.3	0.003	
σ_1	0.009	-					
R_2	3.91	0.013	Gd				
N_2	1.95	0.38					
σ_2	0.011	-					
Gd L_3 edge of Pt_5Gd (10 nm) subjected to electrochemical cycling							
Variable	**Value**	**Error**	**Atom**	k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-		3	10	1.4	3.4
e_0	3.97	9.42					
R_1	2.28	0.08	O	χ^2	Red(χ^2)	*R*-factor	
N_1	2.05	0.59		292.5	79.3	0.156	
σ_1	0.009	-					
R_2	2.95	0.06	Pt				
N_2	2.28	0.80					
σ_2	0.006	-					

Table S4. EXAFS data of Pt_5Gd (10 nm) sample after electrochemical cycling taken at 0.2°.

Pt L_3 edge of Pt_5Gd (10 nm) subjected to electrochemical cycling								
Variable	**Value**	**Error**	**Atom**		k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-			3	14	1.9	3.2
e_0	8.11	0.95						
R_1	2.74	0.006	Pt		χ^2	Red(χ^2)	*R*-factor	
N_1	8.39	0.44			589.7	98.5	0.016	
σ_1	0.009	-						

Table S5. EXAFS data of as-prepared $Pt_{7.5}Gd$ (10 nm) sample taken at 2°.

Pt L_3 edge of $Pt_{7.5}Gd$ (10 nm) not subjected to electrochemical cycling							
Variable	**Value**	**Error**	**Atom**	k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-		3	14	1.8	3.4
e_0	7.98	0.36					
R_1	2.73	0.0023	Pt	χ^2	Red(χ^2)	*R*-factor	
N_1	8.66	0.175		378.9	47.91	0.003	
σ_1	0.009	-					
Gd L_3 edge of Pt7.5Gd (10 nm) not subjected to electrochemical cycling							
Variable	**Value**	**Error**	**Atom**	k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-		3	10	1.6	3.4
e_0	13.98	4.33					
R_1	2.39	0.043	O	χ^2	Red(χ^2)	*R*-factor	
N_1	2.40	0.513		535.0	195.5	0.094	
σ_1	0.007	-					
R_2	2.97	0.040	Pt				
N_2	1.31	0.624					
σ_2	0.004	-					

Table S6. EXAFS data of $Pt_{7.5}Gd$ (10 nm) sample after electrochemical cycling taken at 2°.

Pt L_3 edge of $Pt_{7.5}Gd$ (10 nm) subjected to electrochemical cycling							
Variable	**Value**	**Error**	**Atom**	k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-		3	14	1.8	3.4
e_0	8.87	0.43					
R_1	2.75	0.002	Pt	χ^2	Red(χ^2)	*R*-factor	
N_1	9.91	0.23		624.5	105.7	0.003	
σ_1	0.008	-					
R_2	3.44	0.04	Gd (Pt)				
N_2	0.99	0.53					
σ_2	0.01	-					
Gd L_3 edge of $Pt_{7.5}Gd$ (10 nm) subjected to electrochemical cycling							
Variable	**Value**	**Error**	**Atom**	k_{min}	k_{max}	R_{min}	R_{max}
s_{02}	0.90	-		3	10	1.8	3.8
e_0	20.61	2.77					
R_1	2.57	0.02	Pt	χ^2	Red(χ^2)	*R*-factor	
N_1	2.53	0.39		201.9	54.7	0.076	
σ_1	0.004	-					
R_2	3.33	0.077	Gd				
N_2	0.50	0.56					
σ_2	0.004	-					

Table S7. Overview of the fitted data (from table S1-S6). Note a overlayer volume fraction of 0.6 have been employed to discern overlayer strain.

		Nearest Pt-Pt distance		**Nearest Pt-Pt strain**		**Overlayer Pt-Pt distance/strain**
Sample		As-prepared	After electrochemistry	As-prepared	After electrochemistry	After electrochemistry
Pt foil@2.0°		2.78 Å	-	0	-	-
Pt_5Gd@0.2°		-	2.74 Å	-	-1.18	-
Pt_5Gd@2.0°		2.69 Å	2.73 Å	-3.11	-1.57	2.76 Å/-0.54
$Pt_{7.5}Gd$@2.0°		2.73 Å	2.75 Å	-1.57	-0.83	2.77 Å/-0.34

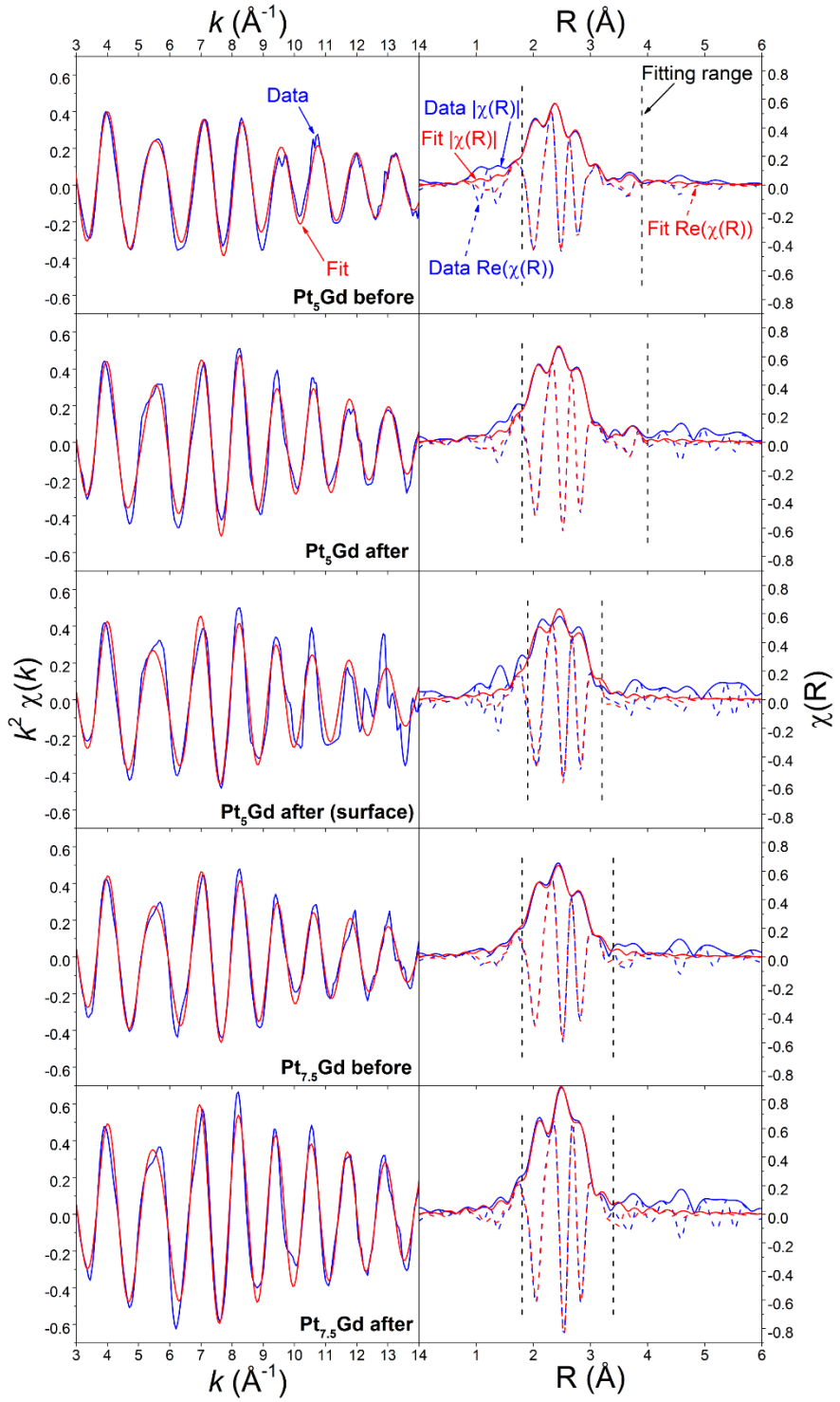

Figure S1. k^2-weighted EXAFS oscillation function plotted *vs.* the wavenumber (left) and real-space Fourier transform *vs.* lattice spacing (right) of the Pt L_3 edge for 10 nm Pt_5Gd and $Pt_{7.5}Gd$ thin films before and after electrochemical cycling.

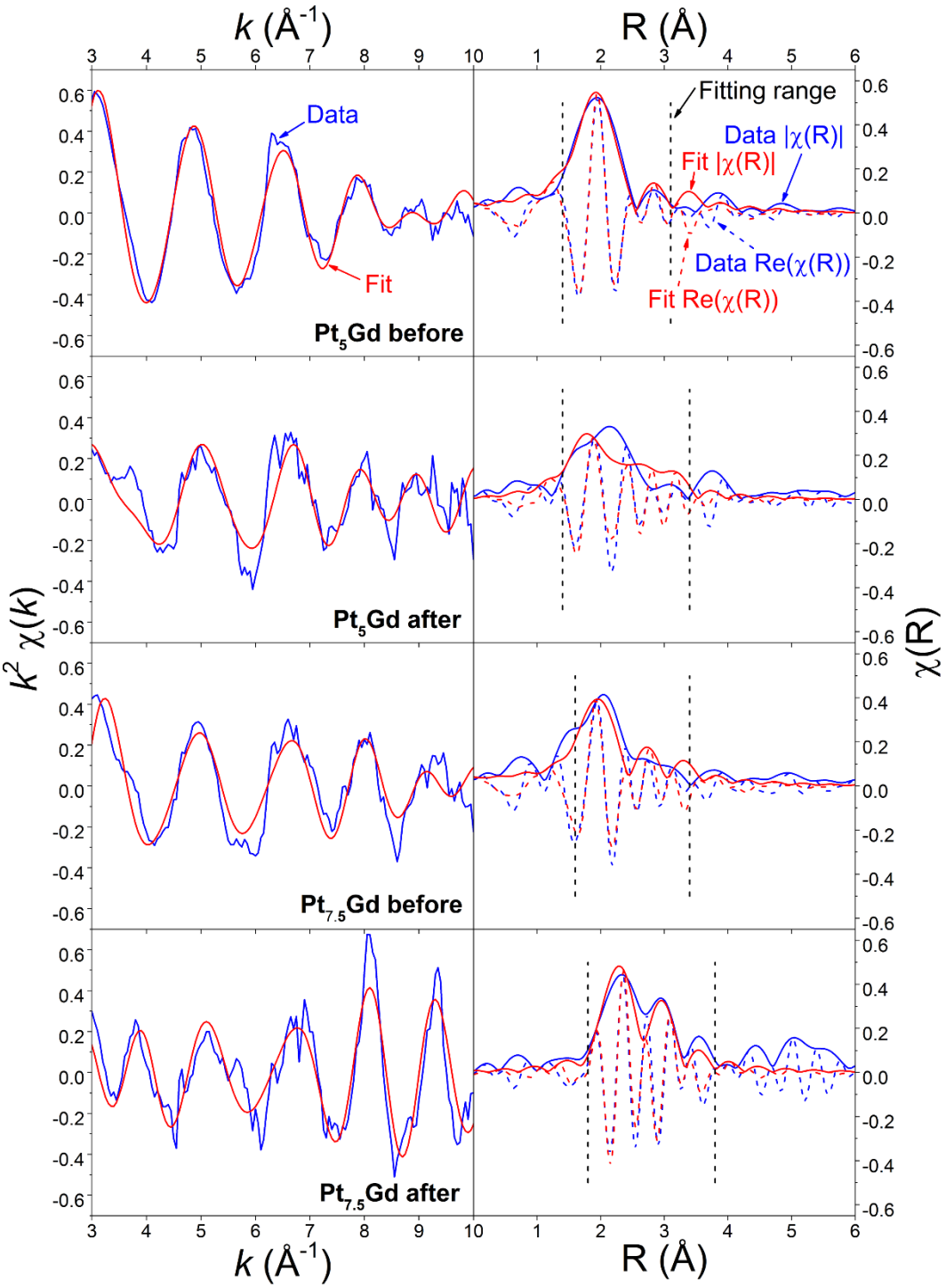

Figure S2. k^2-weighted EXAFS oscillation function plotted *vs.* the wavenumber (left) and real-space Fourier transform *vs.* lattice spacing (right) of the Gd L_3 edge for 10 nm Pt_5Gd and $Pt_{7.5}Gd$ thin films before and after electrochemical cycling.

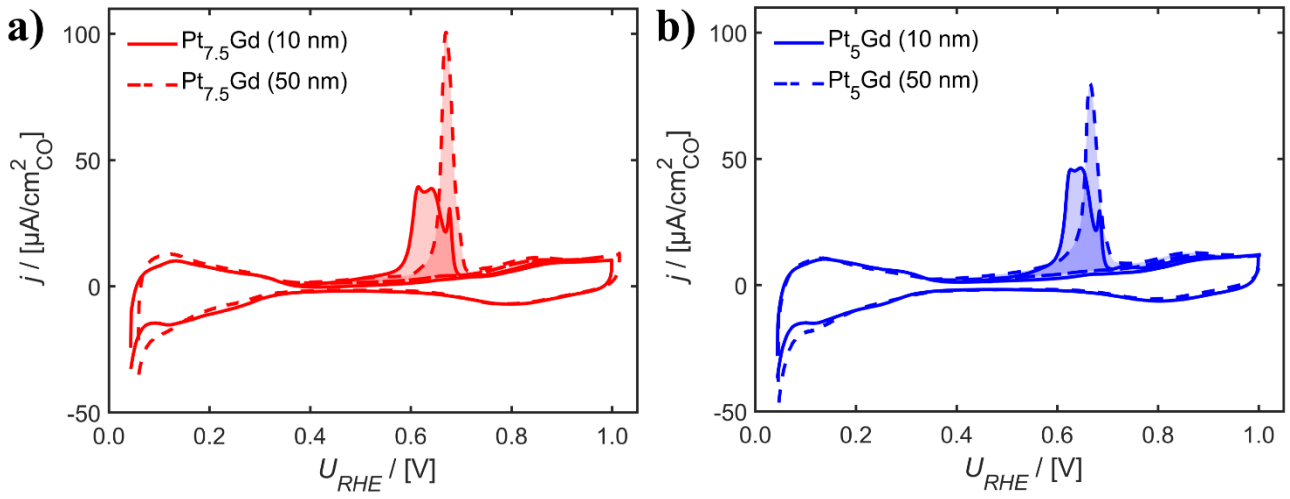

Figure S3. CO-stripping CVs of 10 and 50 nm thin films samples in Ar-saturated 0.1 M $HClO_4$ at room temperature, 200 rpm and 10 mV/s; **a)** $Pt_{7.5}Gd$; **b)** Pt_5Gd. Note currents have been normalised with the CO stripping area.

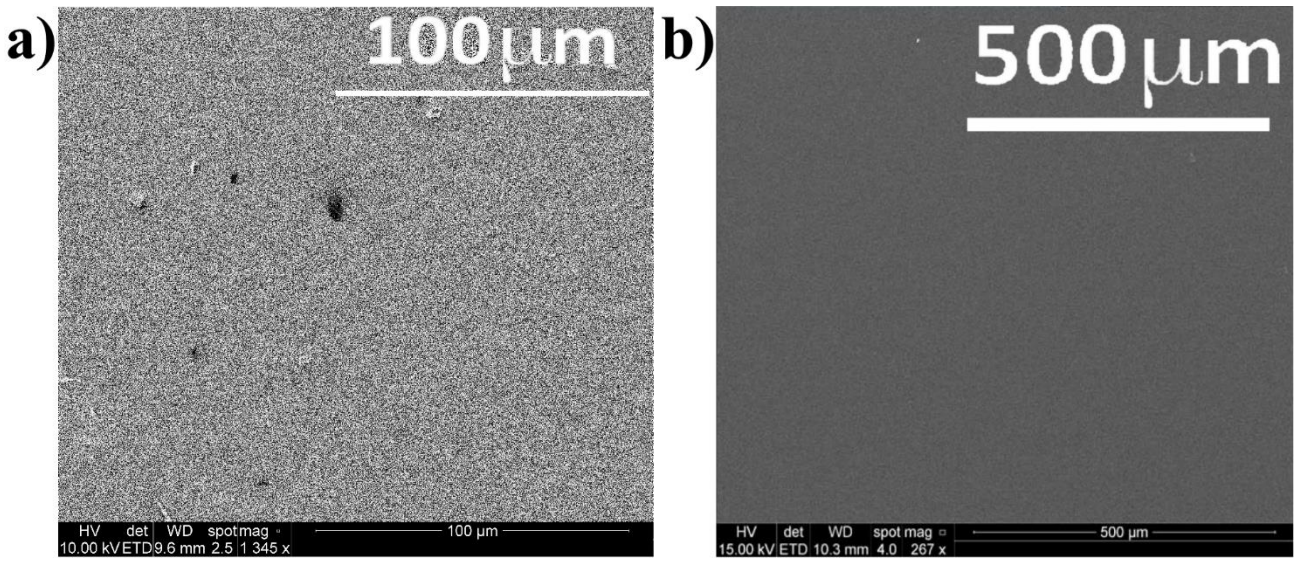

Figure S4. Example SEM images of thin films with **a)** and without **b)** pin-holes formed [2].

References

1. Velázquez-Palenzuela, A.; Masini, F.; Pedersen, A. F.; Escudero-Escribano, M.; Deiana, D.; Malacrida, P.; Hansen, T. W.; Friebel, D.; Nilsson, A.; Stephens, I. E. L.; Chorkendorff, I. The enhanced activity of mass-selected PtxGd nanoparticles for oxygen electroreduction. *J. Catal.* **2015**, *328*, 297–307, doi:10.1016/j.jcat.2014.12.012.
2. Zamburlini, E.; Jensen, K. D.; Stephens, I. E. L.; Chorkendorff, I.; Escudero-Escribano, M. Benchmarking Pt and Pt-lanthanide sputtered thin films for oxygen electroreduction: fabrication and rotating disk electrode measurements. *Electrochim. Acta* **2017**, *247*, 708–721, doi:10.1016/j.electacta.2017.06.146.