Fundamental insight into enhanced activity of Pd/CeO_2 thin films in hydrogen oxidation reaction in alkaline media

Supporting information

Authors: Mathilde Luneau[1, 2]*, Linnéa Strandberg[2], Gerard Montserrat-Sisó[2], Victor Shokhen[2], Roopathy Mohan[2], Henrik Grönbeck[2], Björn Wickman[2]

1. Department of Chemistry and Chemical Engineering and Competence Centre for Catalysis, Chalmers University of Technology, Gothenburg, SE 41296 (Sweden)
2. Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, Gothenburg, SE 41296 (Sweden)

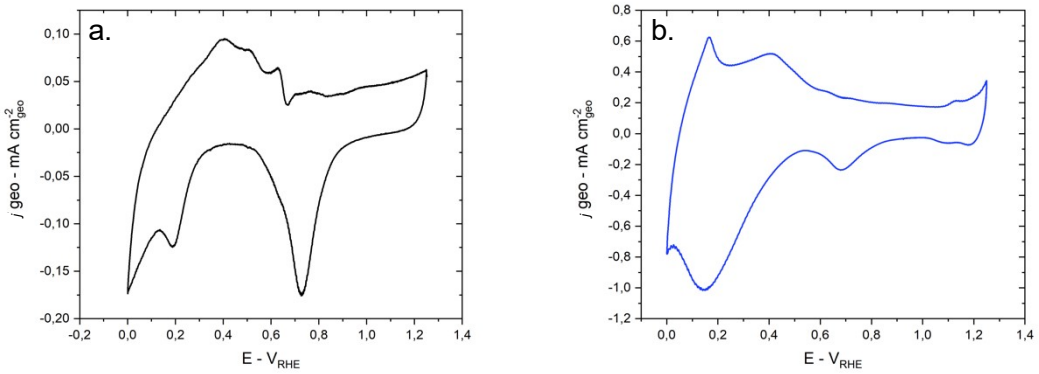

Figure S1: CV at $50mV.s^{-1}$ during conditioning on a. pure Pd quartz crystal b. Pd/CeO_2 quartz crystal

Table S1: ECSA measured on glassy carbon electrodes and quartz crystals before and after reaction

Methods			**GCE**		**QCM**	
			Pd	Pd/CeO_2	Pd	Pd/CeO_2
Pd oxides reduction	ECSA before HOR (cm^2_{Pd})		0.40 ± 0.01	0.41 ± 0.01	0.35 ± 0.01	0.35 ± 0.1
	ECSA after HOR (cm^2_{Pd})		0.36 ± 0.01	0.37 ± 0.01	/	/
CO stripping	ECSA after HOR (cm^2_{Pd})	run 1	/	/	0.39 ± 0.01	0.34 ± 0.01
		run 2	/	/	0.34 ± 0.01	0.34 ± 0.01
		run 3	/	/	0.36 ± 0.01	0.35 ± 0.01

Table S2: Comparison of specific activity with other published results

	Specific activity at 0.1 V_{RHE} j – mA cm^{-2}_{Pd}	**Reference**
Pd thin film	0.003	This work
Pd/CeO_2 thin film	0.122	This work
Pd black	0.002	Yarmiayev et al. *
7% ceria-doped Pd black	0.051	Yarmiayev et al. *
11% ceria-doped Pd black	0.14	Yarmiayev et al. *

** Yarmiayev et al 2019 J. Electrochem. Soc. 166 F3234, measurements performed at 900 rpm*

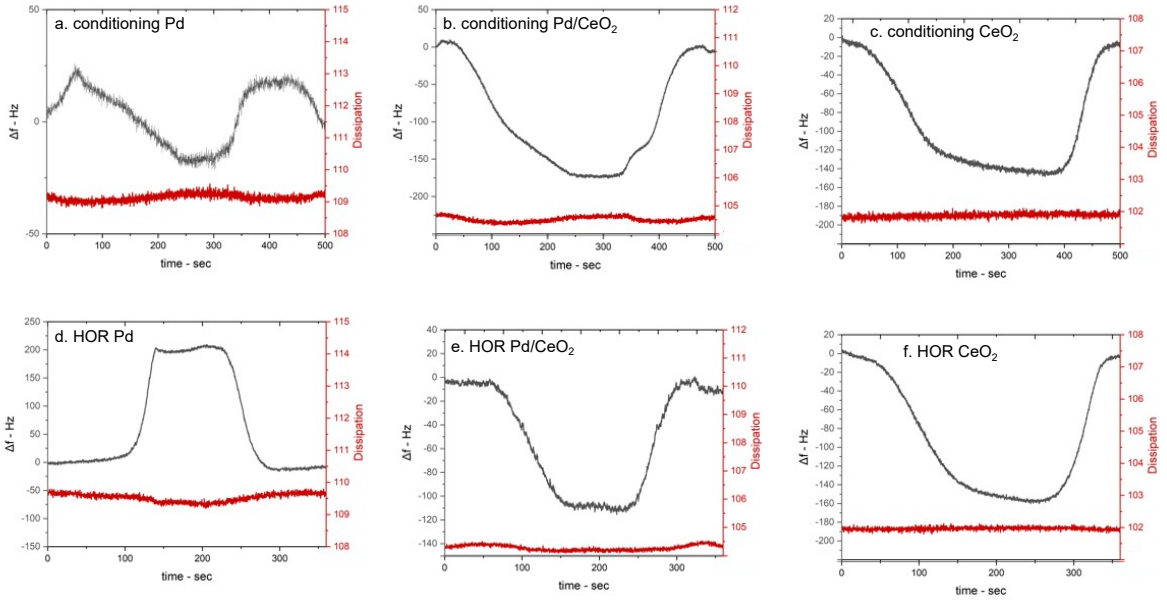

Figure S2: Dissipation measurements during conditioning and HOR on Pd, Pd/CeO_2 and CeO_2 only.

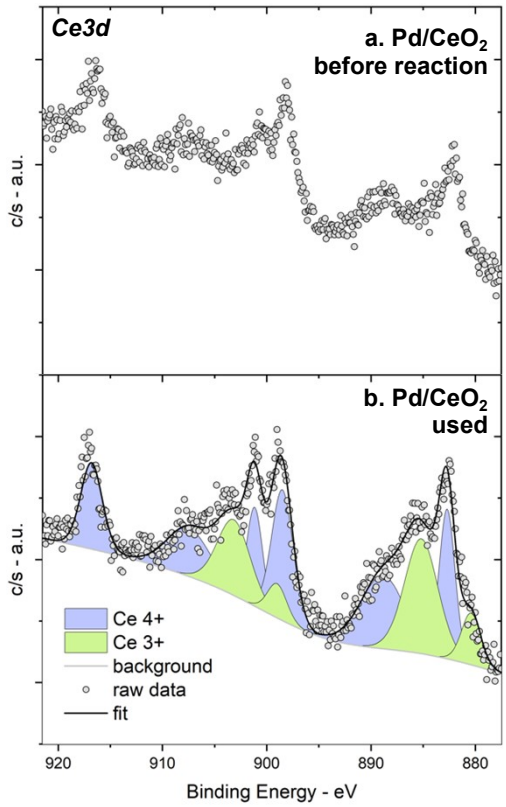

Figure S3: XPS spectra of the Ce3d region measured before (a) and after (b) reaction showing characteristic peaks of Ce^{4+} species in three doublets, as well as of Ce^{3+} species in two doublets.

Table S3: Surface composition of Pd/CeO_2 as measured by XPS before and after HOR

	Binding energy	Before HOR	After HOR
Pd	334.8 ± 0.1 eV	55 %	38%
Pd-O	336 ± 0.1 eV	22%	43%
Pd-O-Ce	337.5 ± 0.1 eV	23%	19%
Areas ratio* $Pd3d_{5/2}/(Pd3d_{5/2}+Ce3d)$		0.89 ± 0.01	0.61 ± 0.01

** The total areas were used and were not corrected with relative sensitivity factors.*

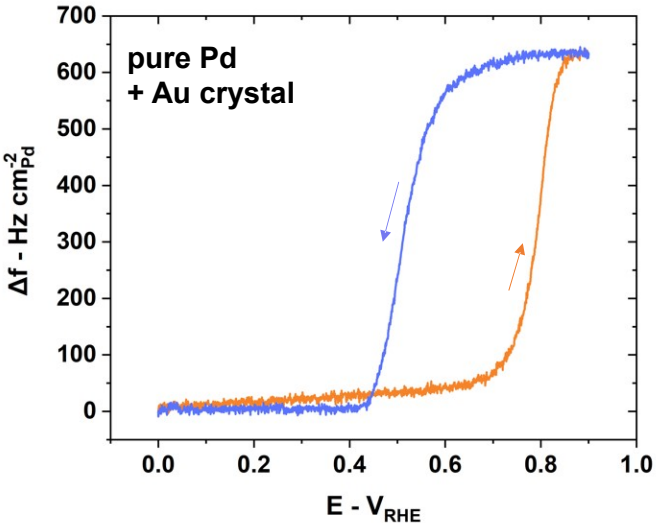

Figure S4: E-QCM measurements performed during HOR on pure Pd thin films deposited on a Au layer (similar to Pd/CeO_2 and CeO_2 crystals)

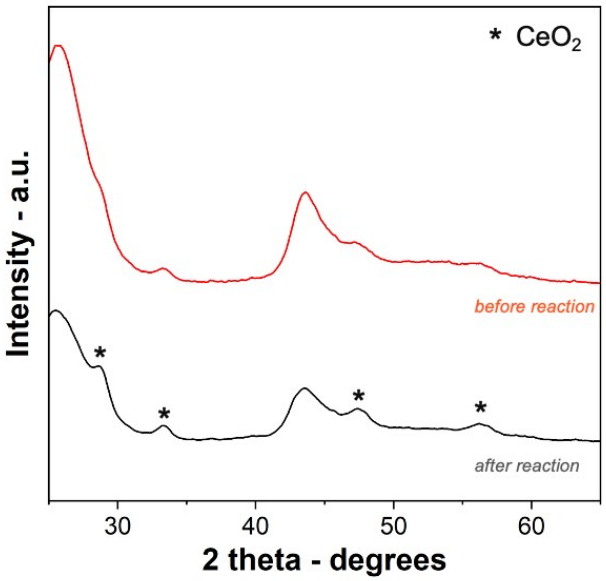

Figure S5: WAXS measurements of Pd/CeO_2 before and after reaction confirm the presence of a CeO_2 phase (ref for CeO_2: Swatsitang et al., Physica B, 2016, 485, 14-20).

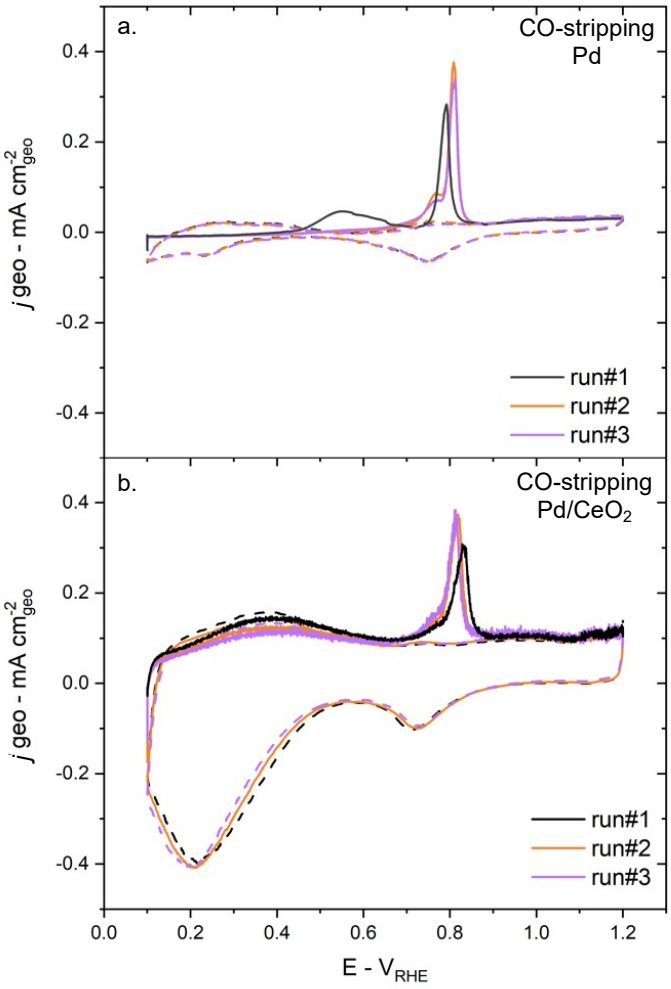

Figure S6: CO-stripping performed on a. Pd and b. Pd/CeO_2 directly after HOR reaction

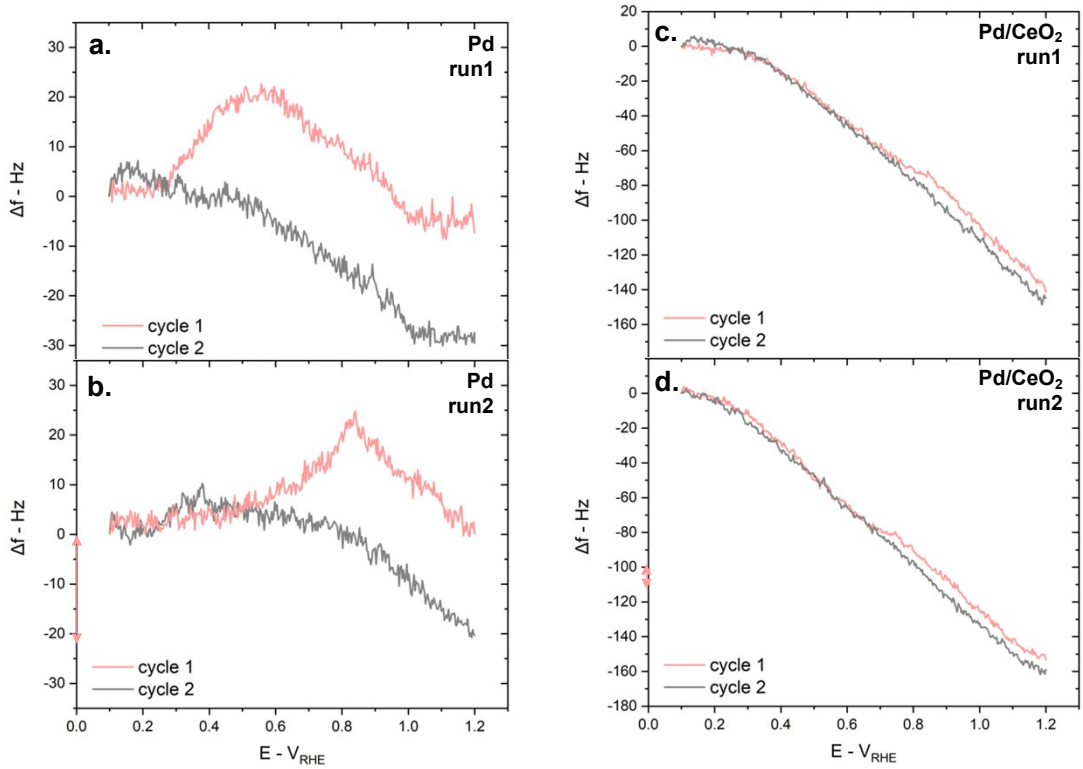

Figure S7: E-QCM measurements during CO-stripping on a. b. Pd and c. d. Pd/CeO_2