

Online Research @ Cardiff

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <http://orca.cf.ac.uk/98352/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Pizzutilo, Enrico, Geiger, Simon, Freakley, Simon J., Mingers, Andrea, Cherevko, Serhiy, Hutchings, Graham John and Mayrhofer, Karl J.J. 2017. Palladium electrodisolution from model surfaces and nanoparticles. *Electrochimica Acta* 229 , pp. 467-477. 10.1016/j.electacta.2017.01.127
filefile

Publishers page: <http://dx.doi.org/10.1016/j.electacta.2017.01.127>
<<http://dx.doi.org/10.1016/j.electacta.2017.01.127>>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



1 **Palladium electrodisolution from model surfaces and**
2 **nanoparticles**

3
4 Enrico Pizzutilo^{a*}, Simon Geiger^a, Simon J. Freakley^b, Andrea Mingers^a, Serhiy
5 Cherevko^{a,c}, Graham J. Hutchings^b, Karl J. J. Mayrhofer^{a,c,d*}

6
7 *^aDepartment of Interface Chemistry and Surface Engineering, Max-Planck-Institut für*
8 *Eisenforschung GmbH,*
9 *Max-Planck-Strasse 1, 40237 Düsseldorf, Germany*

10
11 *^bCardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building,*
12 *Park Place, Cardiff, CF10 3AT*

13
14 *^cHelmholtz-Institute Erlangen-Nürnberg for Renewable Energy (IEK-11),*
15 *Forschungszentrum Jülich, Egerlandstr. 3, 91058 Erlangen, Germany*

16
17 *^dDepartment of Chemical and Biological Engineering, Friedrich-Alexander-*
18 *Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany*

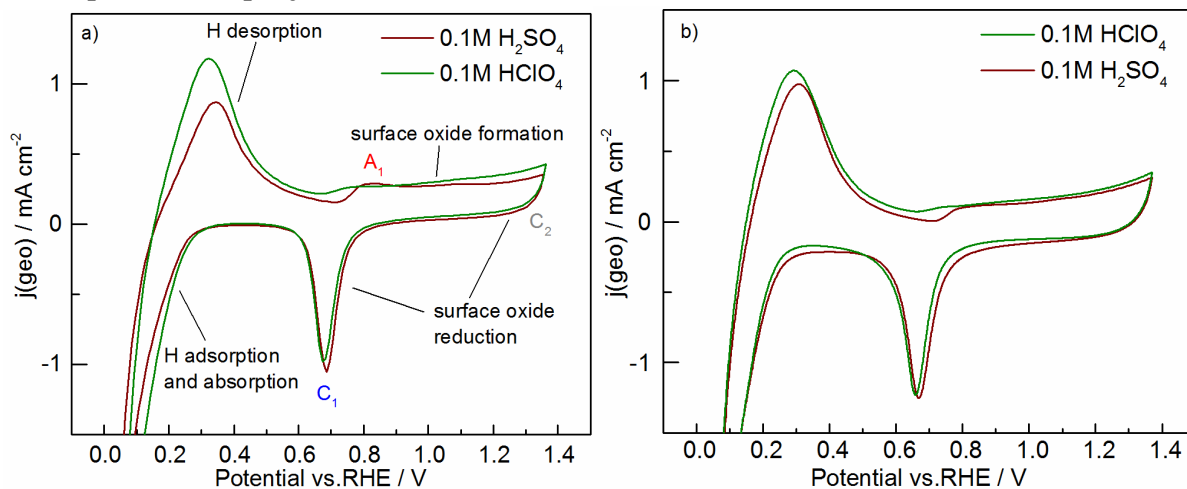
19
20
21 **Corresponding authors: pizzutilo@mpie.de mayrhofer@mpie.de*

22 *Tel.: +49 211 6792 160, FAX: +49 211 6792 218*

25 **SUPPORTING INFORMATION**

26

27 **1 Comparison of poly-Pd CVs in RDE and SFC**

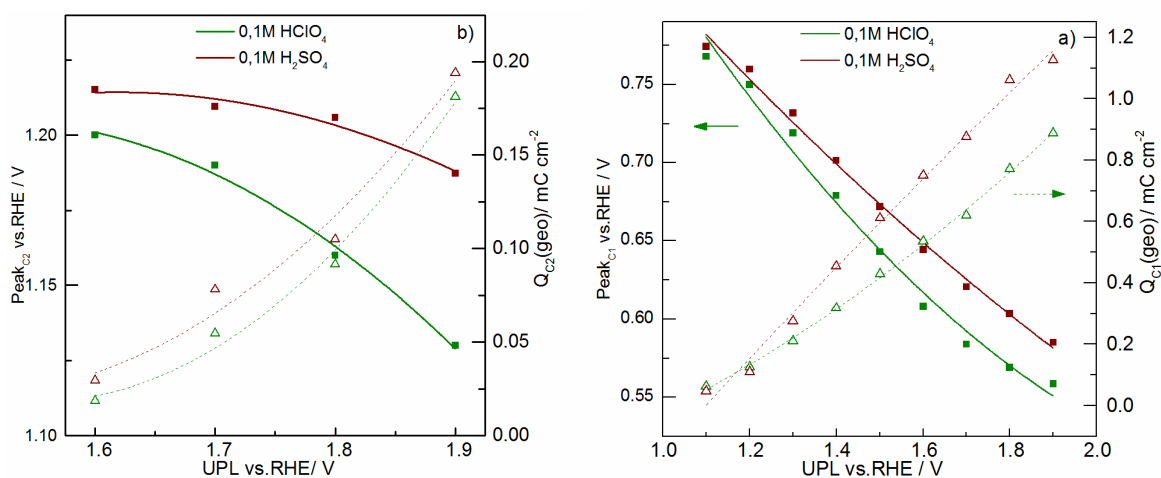


28

29 **Figure S1 CVs taken on a poly-Pd electrode in the SFC(a) and RDE (b) setup in 0.1M**
 30 **HClO₄ and in 0.1M H₂SO₄. Scan rate: 200 mV s⁻¹.**

31 Poly-Pd cyclic voltammograms in deaerated solution (Figure S1) are recorded using
 32 RDE setup with perchloric and sulfuric acid. These CVs validate the results obtained
 33 with the SFC system (shown in Figure 1): classical poly-Pd features including H
 34 absorption and adsorption/desorption, Pd surface oxide formation/reduction are
 35 displayed here. As in SFC, the RDE CVs confirm a slight difference in Pd-oxide formation
 36 onset potential in the two electrolytes due to the diverse anion adsorption [1].

37 **2.1 Poly-Pd reduction peaks with UPL**



38

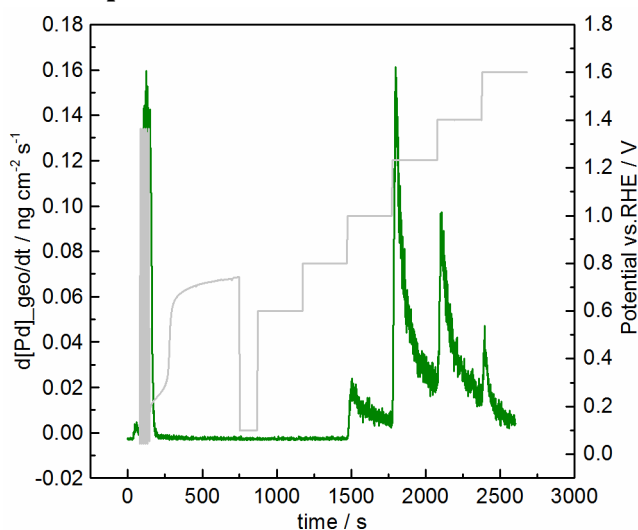
39 **Figure S2.1 (a) Plots of peak potential Peak_{C1} a charge density Q_{C1} of the Pd(II)**
 40 **reduction peak (C₁) as a function of the UPL. (b) Plots of peak potential Peak_{C2} a**
 41 **charge density Q_{C2} of the Pd(IV) reduction peak (C₂) as a function of the UPL. Both**

42 **plots correspond to the poly-Pd cyclic voltammograms in perchloric and sulfuric**
43 **acid shown in Figure 2.**

44 The maximum reduction peak potentials and the calculated charge densities
45 (corresponding to the cathodic scans of the CVs in Figure 2a) of the Pd(II)-oxide
46 reduction peak (C_1) and of the Pd(IV)-oxide reduction peak (C_2) are shown in Figure
47 S2.1. In the literature it is known that increasing the UPL the reduction peak of Pd is
48 shifting to lower potentials as a direct consequence of the different amount of oxide
49 formed[2], even though a clear explanation is not available at present.

50 In the case of Pd(IV)-oxide reduction peak no big difference is observed in the two
51 electrolyte, whereas the position of the Pd(II)-oxide reduction peak in perchloric acid is
52 shifting more to lower potentials compared to the shift in sulfuric acid. In fact, while
53 with an UPL of 1.0 V_{RHE} no difference was observed in the two electrolytes, at much
54 larger UPL the difference in the peak potential increases to almost 50 mV. Similarly the
55 associated Pd(II)-oxide reduction charge is initially the same, while at higher potentials
56 a difference up to ca. 20% in the reduction charge (higher in sulfuric acid) was measured
57 (Figure S2.1). This is probably due to the different interaction of the electrolytes anions
58 with the Pd electrode (see discussion).

59 **2.2 Poly-Pd potentiostatic passivation**



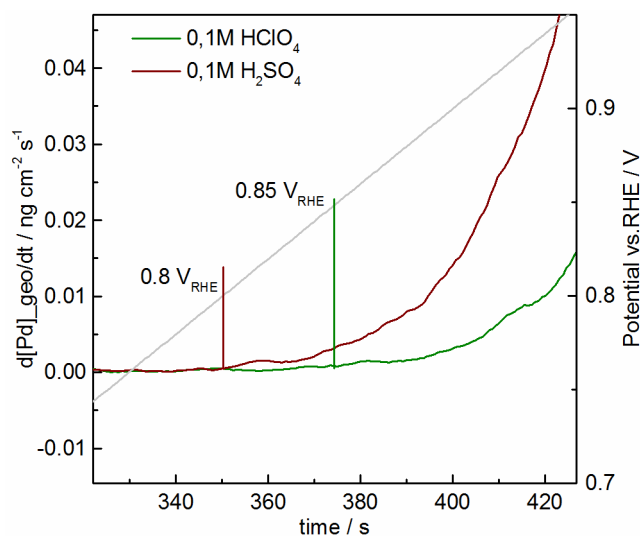
60

61 **Figure S2.2 Potentiostatic dissolution of poly-Pd at different applied potential**
62 **during a potential step experiment (time of each potential step: 300 s).**

63 In Figure S2.2 is reported a measurement of the potentiostatic (steady-state) poly-Pd
64 dissolution. The potential program applied consisted in 30 activation cycles followed by
65 OCP and a series of potential steps of 300 s each with increasing potential from 0.6 to
66 1.6 V_{RHE} (0.2 V for each step). Dissolution is initially observed with potential of 1.0 V_{RHE} .
67 For each step is observed a jump in dissolution, followed by a fast decay, indicating that
68 there is no continue steady-state dissolution. Indeed, with time the oxide is covering and
69 thus passivating the metal surface, resulting in the observed decrease in the dissolution.

70

71 **3 Poly-Pd dissolution onset potential**



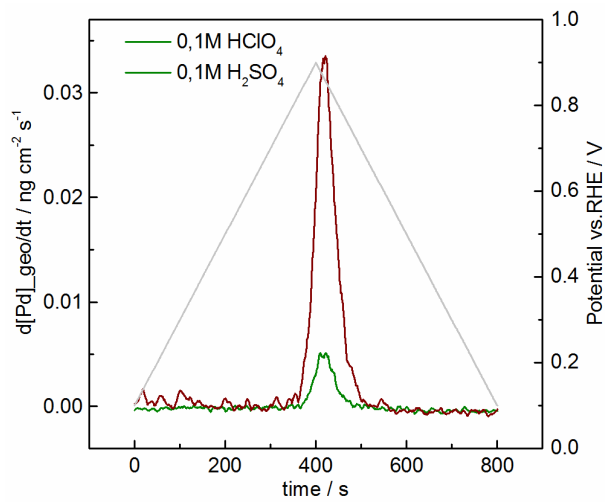
72

73 **Figure S3 Comparison of the poly-Pd dissolution onset potential. Scan rate (2 mV s⁻¹).**
74

75 In Figure S3 is shown a magnification of the poly-Pd dissolution signal collected by the
76 ICP-MS during a positive-sweep at very low scan rate (2 mV s⁻¹). The Pd onset potential
77 is evaluated as the deviation from the background signal. In the two electrolytes, the
78 measured onset potentials appear shifted of approximately 50 mV. This might also be
79 caused by the difference in the dissolution rates of Pd in the two analyzed electrolytes.
80 Indeed, Pd in perchloric acid might also dissolve earlier than measured, but just being
81 below the ICP-MS detection limit.

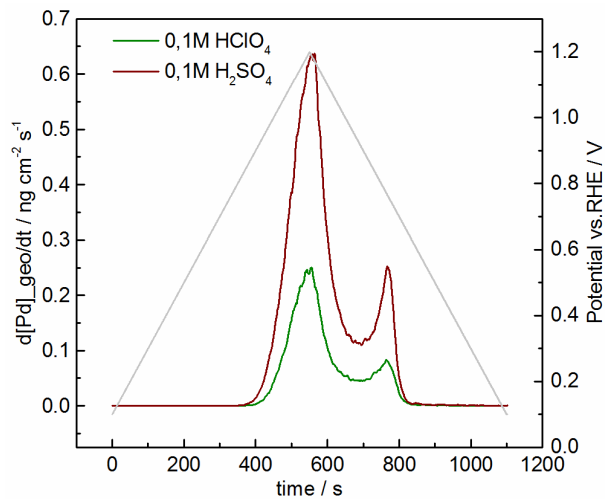
82

83 **4 Poly-Pd dissolution at lower scan rate**



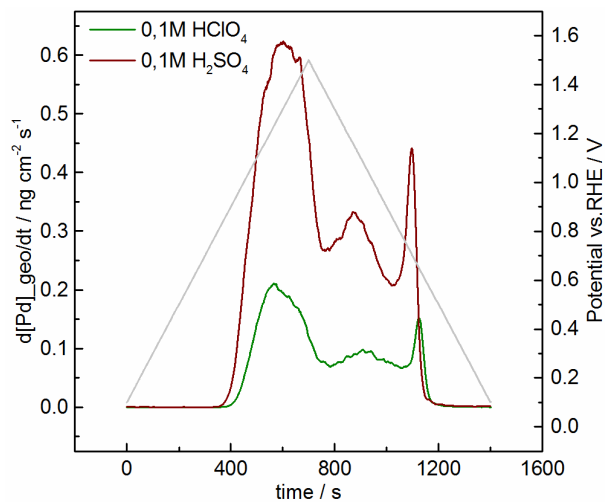
84

85 **Figure S4.1 Poly-Pd dissolution profiles in 0.1M HClO₄ and H₂SO₄ with UPL= 0.9**
86 **V_{RHE}. Scan rate: 2 mV s⁻¹.**



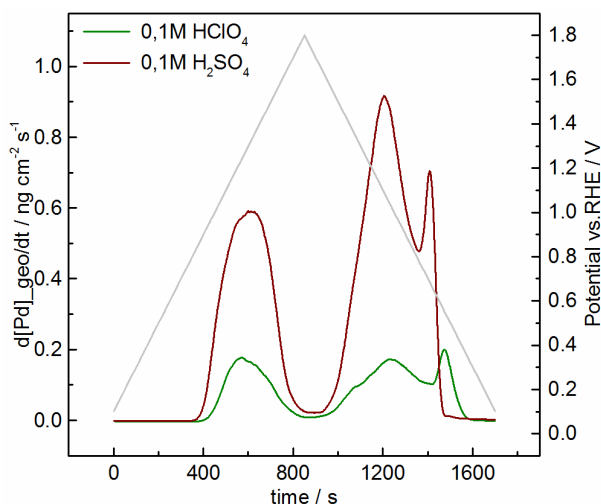
87

88 **Figure S4.2 Poly-Pd dissolution profiles in 0.1M HClO₄ and H₂SO₄ with UPL= 1.2**
89 **V_{RHE}. Scan rate: 2 mV s⁻¹.**



90

91 **Figure S4.3 Poly-Pd dissolution profiles in 0.1M HClO₄ and H₂SO₄ with UPL= 1.5**
 92 **V_{RHE}. Scan rate: 2 mV s⁻¹.**
 93



94
 95 **Figure S4.4 Poly-Pd dissolution profiles in 0.1M HClO₄ and H₂SO₄ with UPL= 1.8**
 96 **V_{RHE}. Scan rate: 2 mV s⁻¹.**
 97

98 In Figure S4.1-4 are shown separately the four CVs and relative dissolution profiles
 99 corresponding to the measurement displayed in Figure 3. The difference in onset
 100 potential is once again evident for the different measurement. The maximum of the
 101 anodic dissolution peak in the two electrolytes matches very well for all the different
 102 UPL, whereas the maximum of the cathodic Pd dissolution peaks, in particular the peak
 103 C₁ are delayed with increasing UPL in the case of perchloric acid. This delay mirrors the
 104 greater shift of the Pd(II)-oxide reduction peaks with UPL observed in the CVs recorded
 105 in perchloric acid (Figure S2.1).

106
 107 The quantitative difference between dissolution in perchloric and sulfuric acid, observed
 108 at faster scan rate (Table 1) is here confirmed (Table S4.1), even though in the case of
 109 slower scan rates the difference appears to be slightly reduced (the dissolution in
 110 sulfuric acid is here only almost 3 times than in perchloric acid, while at faster scan rate
 111 is 5 times).

112 **Table S1 The comparison of amount of Pd in 0.1M H₂SO₄ and Pd* in 0.1M HClO₄**
 113 **dissolved per cycle depending on the applied UPL as derived from potential sweep**
 114 **experiments at 2 mV s⁻¹.**

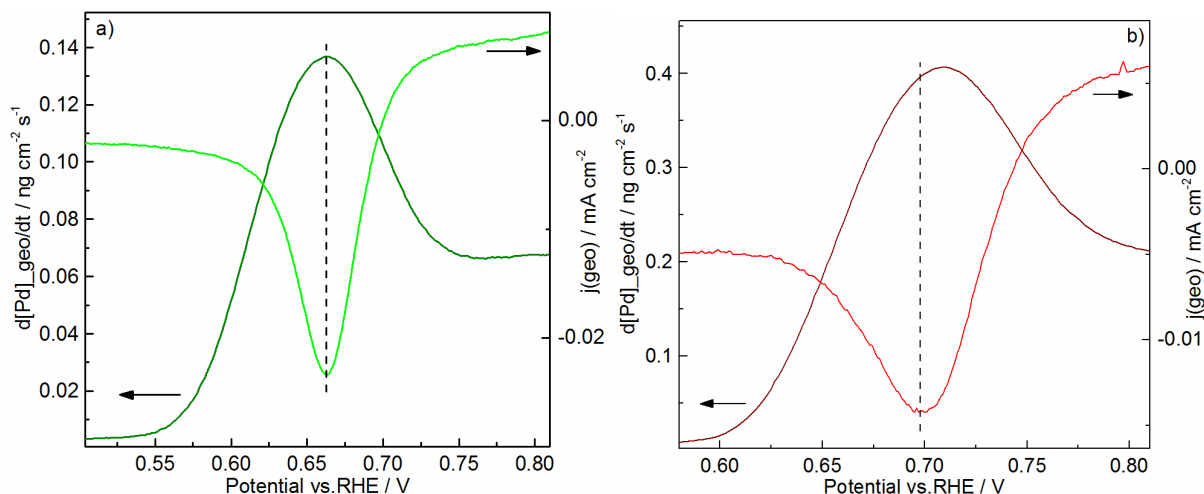
UPL / V _{RHE}	Pd / ng cm _{geo} ⁻² cycle ⁻¹	Pd* / ng cm _{geo} ⁻² cycle ⁻¹
0.9	1.5	0.06
1.2	98.8	36.9
1.5	259.6	80.8
1.8	429.6	106.3

115

116 5 Poly-Pd mass CVs

117

118 In Figure S5.1 are shown the mass cyclic voltammograms corresponding to the poly-Pd
119 dissolution profiles shown in Figure 3. The arrows indicate the positive and negative
120 scan for the Pd mass cyclic voltammograms with 1.8 V_{RHE} UPL. The cathodic dissolution
121 maxima are shifting to lower potentials with increasing UPL, accordingly to the
122 thickness of the formed Pd oxide and thus to the shift in reduction peak [2].



123

124 **Figure 5 Correlation between cathodic dissolution and Pd(II)-oxide reduction**
125 **signals in perchloric (a) and sulfuric acid (b). UPL: 1.5 V_{RHE}. Scan rate: 2 mV s⁻¹.**

126

127 6 Pd/C

128

129 From the statistical average particle size and the loading a total initial surface area per
130 printed layer of 0.31 mm² is calculated (A_s in Table S2).

	median / nm	mean / nm	st. dev.	ECSA* / m ² g ⁻¹	A _s (1l)** / mm ²
Pd	3.7	4.0	±1.3	124	0.31

*ECSA refers to the catalyst specific surface area, that was calculated from the particle mean size; **A_s refers to the total surface area of per deposited layer (≈2.5 ng)

131 **Table S2 Particle size and specific surface area of the Pd/C catalyst investigated in**

132

133 The surface area of the Pd/C nanocatalyst is estimated from the TEM average sizes
134 following the calculation described in [2]. In our case a spherical geometry was assumed,
135 whose volume is:

136

$$V = \frac{4}{3} \pi r^3 \quad S1.1$$

137

138 Where r is the radius (half of the mean particle size as in Table S2).

139

139 The surface area is:

140

$$A = 4 \pi r^2 \quad S1.2$$

141

142 Thus, the specific surface area is:

143

$$ECSA = \frac{3}{(r \cdot \rho)} \quad S1.3$$

144

145 Where ρ is the crystallographic density of palladium ($\rho_{Pd} = 12.02 \text{ g cm}^{-3}$):

146

146 The total metal surface area was calculated as follow:

147

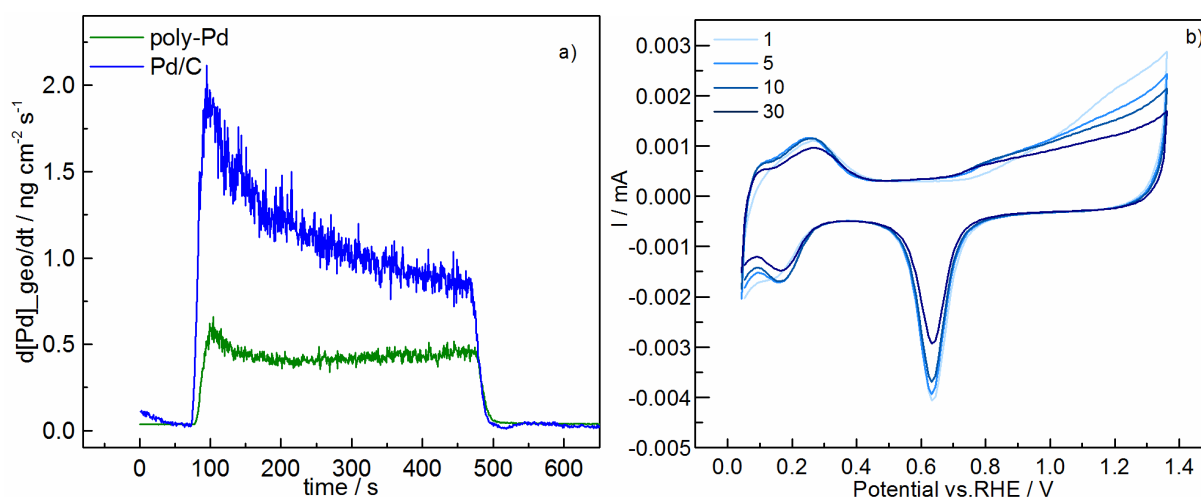
$$A_s = ECSA \cdot m \quad S1.4$$

148

149 Where m is the mass of metal ($2.5 \text{ ng}_{\text{metal}}$)

150

151



152

153 **Figure S6.1 Dissolution profiles of poly-Pd and supported Pd/C nanoparticles**
 154 **during 30 activation cycles with a scan rate of 200 mV s^{-1} (a) and the**
 155 **corresponding cyclic voltammograms of the Pd/C electrode (b) in SFC. The Pd/C**
 156 **dissolution signal was normalized with the surface area after activation.**

157

157 The CVs of the activation cycles and the associated dissolution are shown in Figure S6.1.

158

158 In contrast with poly-Pd the dissolution rate of Pd/C is steadily decreasing. This is due to

159

159 the fact that, unlike for bulk material, the dissolution of nanoparticles along with other

160

160 degradation mechanisms lead to a decrease in surface area, evident from a comparison

161

161 between the first and the last CVs of the activation protocol (Figure S6.1 b). Note that the

162

162 dissolution profile for Pd/C has been normalized with the surface area of the last

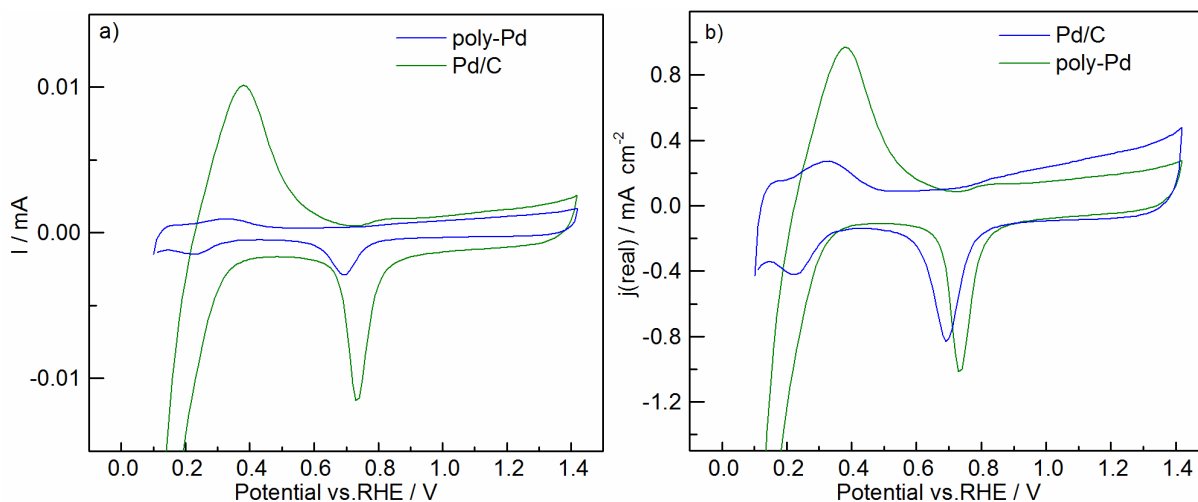
163

163 activation cycle that corresponds to the initial TEM area minus the difference in the Pd

164

164 oxide reduction peak (decrease of the total surface area of approximately 35%).

165 The poly-Pd and Pd/C last activation cycles were also compared (Figure S6.2). The Pd/C
 166 reduction peak is much lower than that of poly-Pd (0.00148 and 0.00460 mC
 167 respectively).



168

169

170 **Figure S6.2 Last CVs of the activation cycle taken on a poly-Pd and Pd/C electrode**
 171 **in the SFC setup (normalized in b). Scan rate: 200 mV s⁻¹.**

172

173 **Table S3 Calculated charges of Pd-oxide reduction peaks and corresponding**
 174 **calculated areas using 424 $\mu\text{C cm}^{-2}$ as reduction charge per unit area.**

CV	Charge (μC)	Area (cm^2)
Initial Pd/C	2.28	0.0054
Activated Pd/C	1.48	0.0035
Activated poly-Pd	4.6	0.0109

175

176

177

178

179

180 [1] T. Solomun, The Role of the Electrolyte Anion in Anodic-Dissolution of the Pd(100)
 181 Surface, *J Electroanal Chem*, 302 (1991) 31-46.

182 [2] M. Grdeń, M. Łukaszewski, G. Jerkiewicz, A. Czerwiński, Electrochemical behaviour of
 183 palladium electrode: Oxidation, electrodisolution and ionic adsorption, *Electrochim*
 184 *Acta*, 53 (2008) 7583-7598.

185