Supplementary information:

# New Insights Into Corrosion of Ruthenium and Ruthenium Oxide Nanoparticles in Acidic Media

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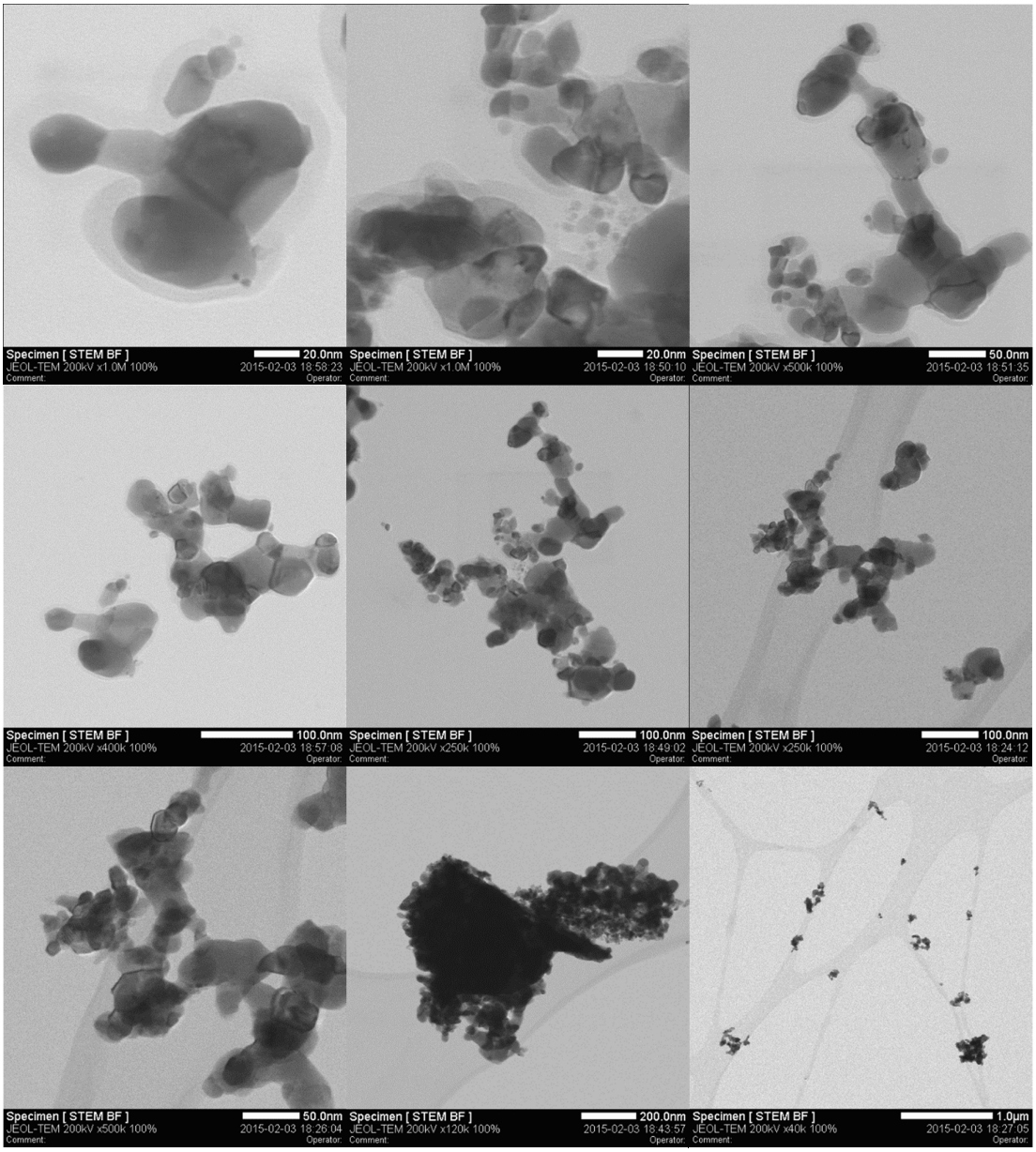



Figure S1: TEM (bright field) images of Ru nanoparticles.

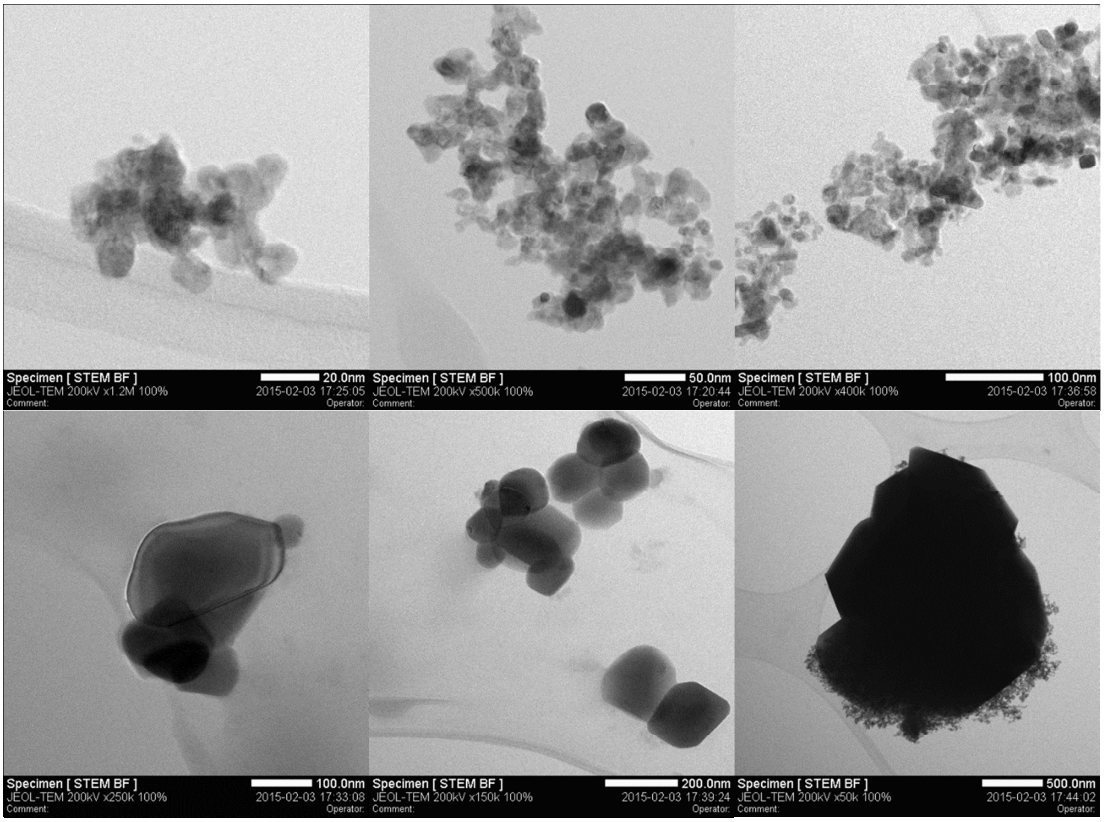
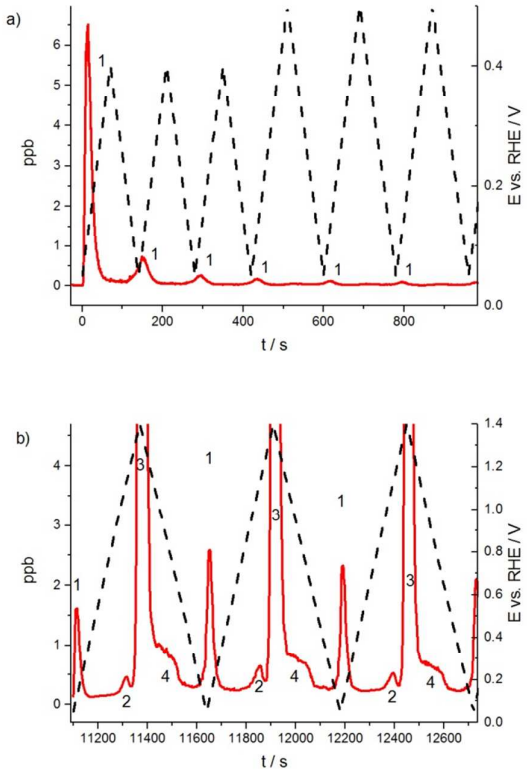
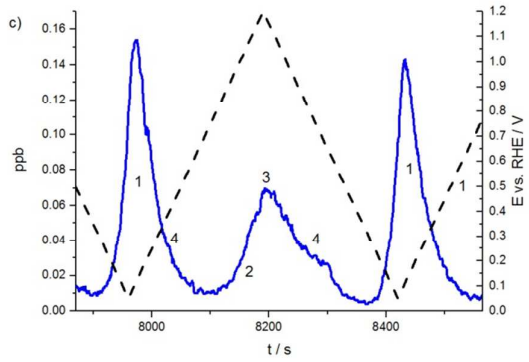
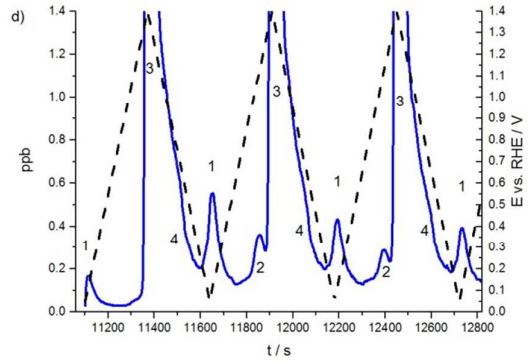



Figure S2: TEM (bright field) images of $RuO_2$ nanoparticles.




c)
ppb
E vs. RHE / V
t / s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E vs. RHE / V
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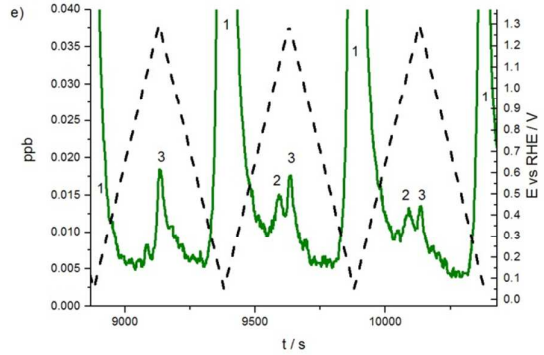
e)
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E vs RHE / V
t / s

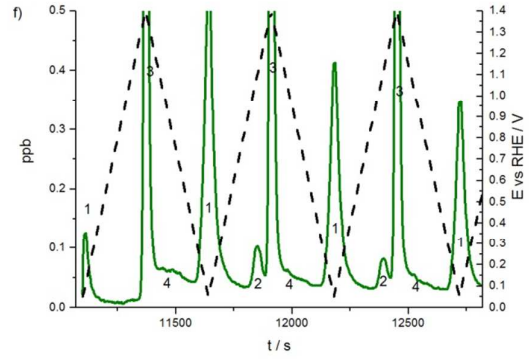

f)
ppb
E vs RHE / V
t / s

Figure S3: Potential resolved ruthenium electrochemical dissolution of as-synthesised Ru (a - initial cycles, b – 3 cycles till 1.4 V), el. $RuO_2$ (c – 1 cycle till 1.2 V, d – 3 cycles till 1.4 V) and th. $RuO_2$ (e – 3 cycles till 1.3 V, f – 3 cycles till 1.4 V) nanoparticles in 0.1 M $HClO_4$ with a sweep rate of 5 mV/s.

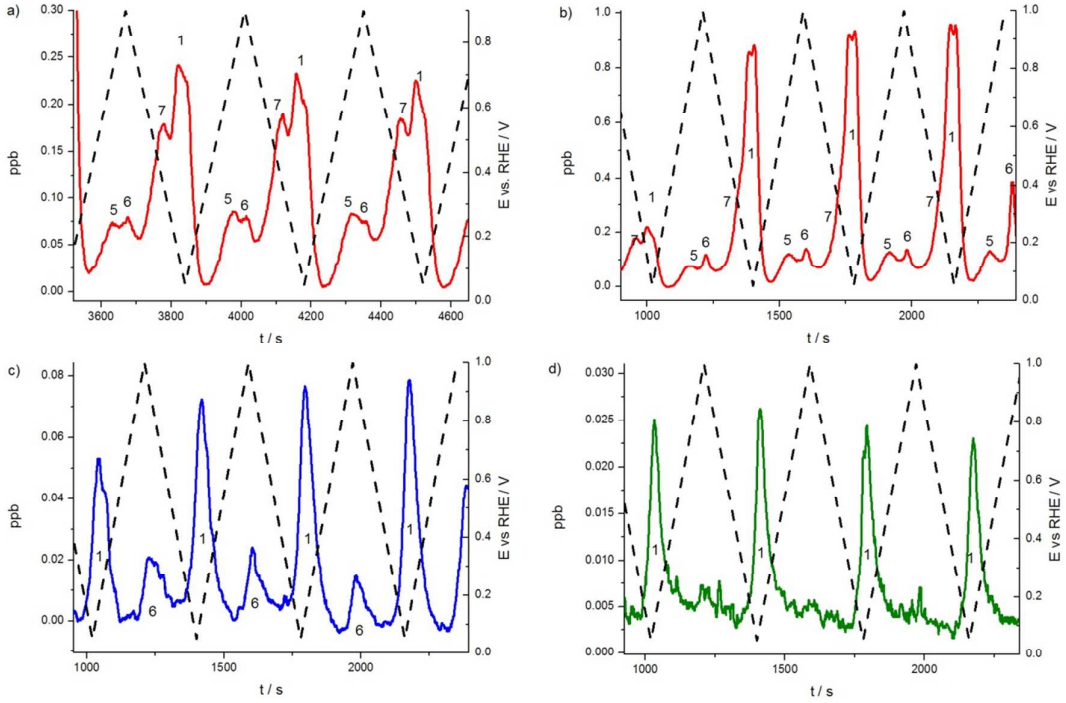



Figure S4: Potential resolved ruthenium electrochemical dissolution with upper potential limit of 1.0 V only for as-synthesised Ru (a) and 1.1 V vs. RHE for of as-synthesised Ru (b), el. $RuO_2$ (c) and th. $RuO_2$ (d) nanoparticles in 0.1 M $HClO_4$ with a sweep rate of 5 mV/s.

Table S1: 4 characteristic features in Ru electrochemical dissolution profile with the potential limit of 1.3 V and 1.4 V that can be assigned to different ruthenium redox processes.

| Peak | Process | Reaction | Potential or $E_o$ = |
|---|---|---|---|
| 1 | Transient dissolution: Reduction of "irreversible" $RuO_x$ | $RuO_x + 2xH^+ + 2xe^- = Ru + xH_2O$ | 0.2 - 0 V vs. RHE |
| 5 | Direct electrochemical dissolution | $Ru = Ru^{2+} + 2e^-$ | 0.455 V + $0.0295\log(Ru^{2+})$ [1] |
| 6 | Transient dissolution | $2Ru + 3\,H_2O = Ru_2O_3 + 6H^+ + 6e^-$ | 0.738 V – 0.0591pH |
| 7 | Transient dissolution: (reduction of "reversible" $RuO_x$) presumably $Ru_2O_3$ or Direct electrochemical dissolution | $Ru_2O_3 + 6H^+ + 6e^- = 2Ru + 3\,H_2O$<br>$RuO_2 = Ru^{3+}$ | 0.738 V – 0.0591pH<br>0.5 V [2-3] |

Possible further dissolution reactions:

When a $RuO_x$ crystal structure gets perturbed by oxidation processes above 1.12 V so that pure underlying Ru gets exposed to the electrolyte (via cracks) the following reactions can occur:

$Ru + 4H_2O = RuO_4^{2-} + 8H^+ + 6e^-$ $E_o = 1.193 – 0.0788pH + 0.0098log(RuO_4^{2-})$

$Ru = Ru^{2+} + 2e^-$ $E_o = 0.455 + 0.0295log(Ru^{2+})$

Ruthenium redeposition could not be measured with our system. Nevertheless, the following reactions can be anticipated [4]:

$2Ru^{2+} + 3H_2O = Ru_2O_3 + 6H^+ + 2e^-$ $E_o = 1.304\ V – 0.1773pH – 0{,}0391log(Ru^{2+})$

$Ru^{2+} + 2H_2O = RuO_2 + 4H^+ + 2e^-$ $E_o = 1.120\ V – 0.1182pH – 0{,}0205log(Ru^{2+})$

Table S2: Ru fraction dissolution amounts (average of 3 cycles):

| % of initial Ru | Ru | El. $RuO_2$ | Th. $RuO_2$ |
|---|---|---|---|
| Cathodic peak 1 1 V | 0.00545 | 0.000185 | 0.00008 |
| All peaks 1 V | 0.00655 | 0.000231 | 0.00009 |
| Cathodic peak 1 1.4 V | 0.0064 | 0.00137 | 0.0013 |
| All peaks 1.4 V | 0.1378 | 0.0222 | 0.0036 |

The height of the Ru dissolution peaks is changing (typically lowering) with cycling. This is due to restructuring and reorganization of $RuO_2$ surface. The same effect was also observed by Chervenko et. al. [5].

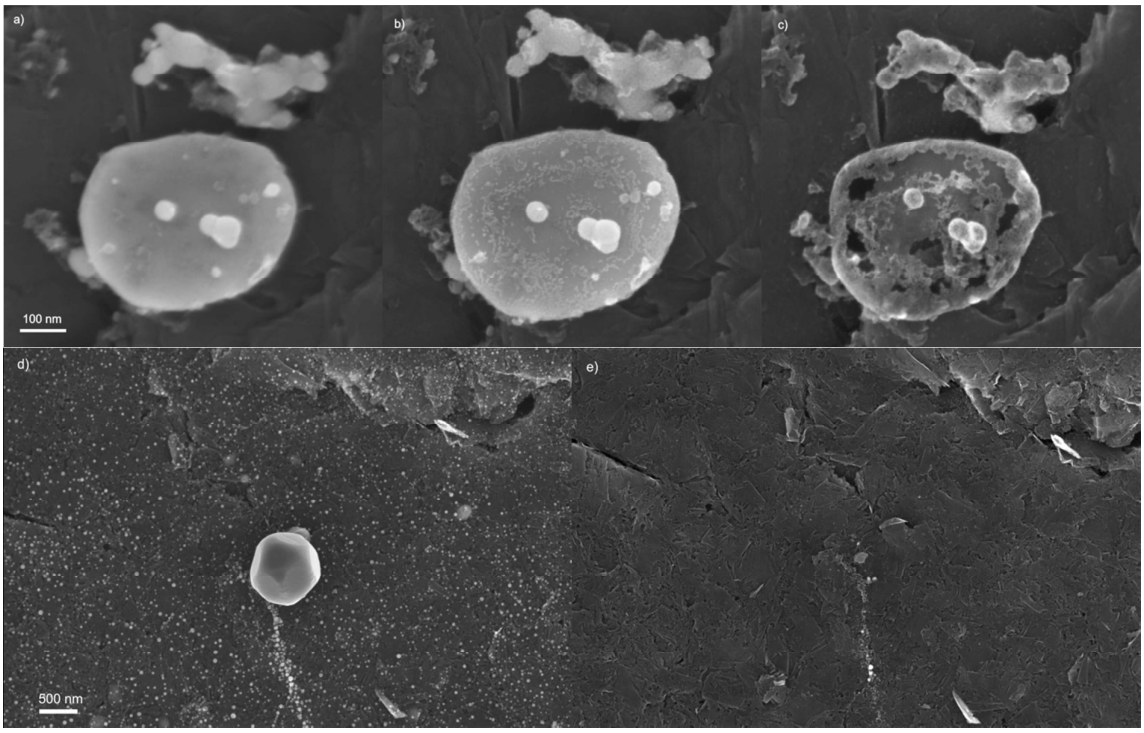


Figure S5: IL-SEM of as-prepared Ru before cycling (a), after 1 cycle (b) and after 2$^{nd}$ (c) cycle from 0.05 to 1.6 V vs. RHE. d) as-prepared Ru and e) Ru after 10 cycles from 0.05 to 1.6 V vs. RHE.

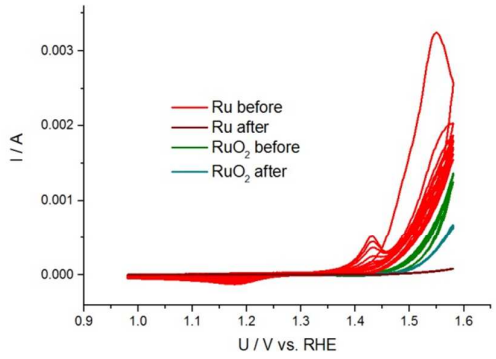



Figure S6: TF-RDE measurements for Ru and th. $RuO_2$ before and after 10000 degradation cycles with 20 mV/s. iR compensation was taken into account.

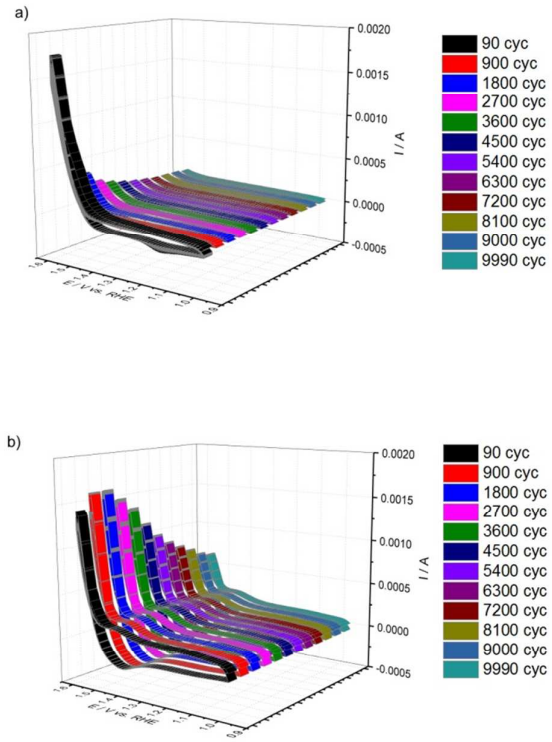



Figure S7: Sequences of 90 TF-RDE OER cycles of a) Ru and b) th. $RuO_2$ in a series of 10000 degradation cycles with 1 V/s. There is no iR compensation included.

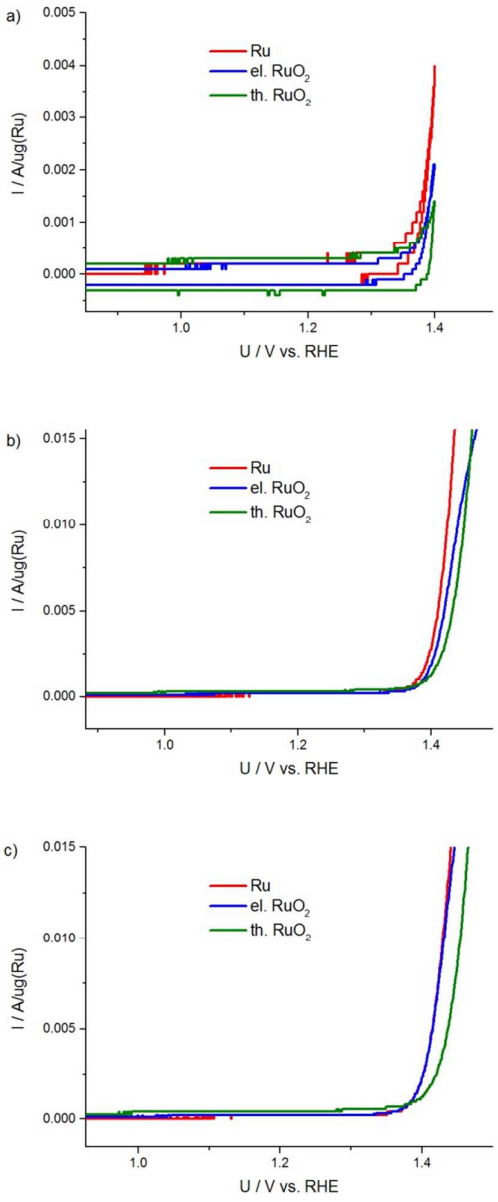
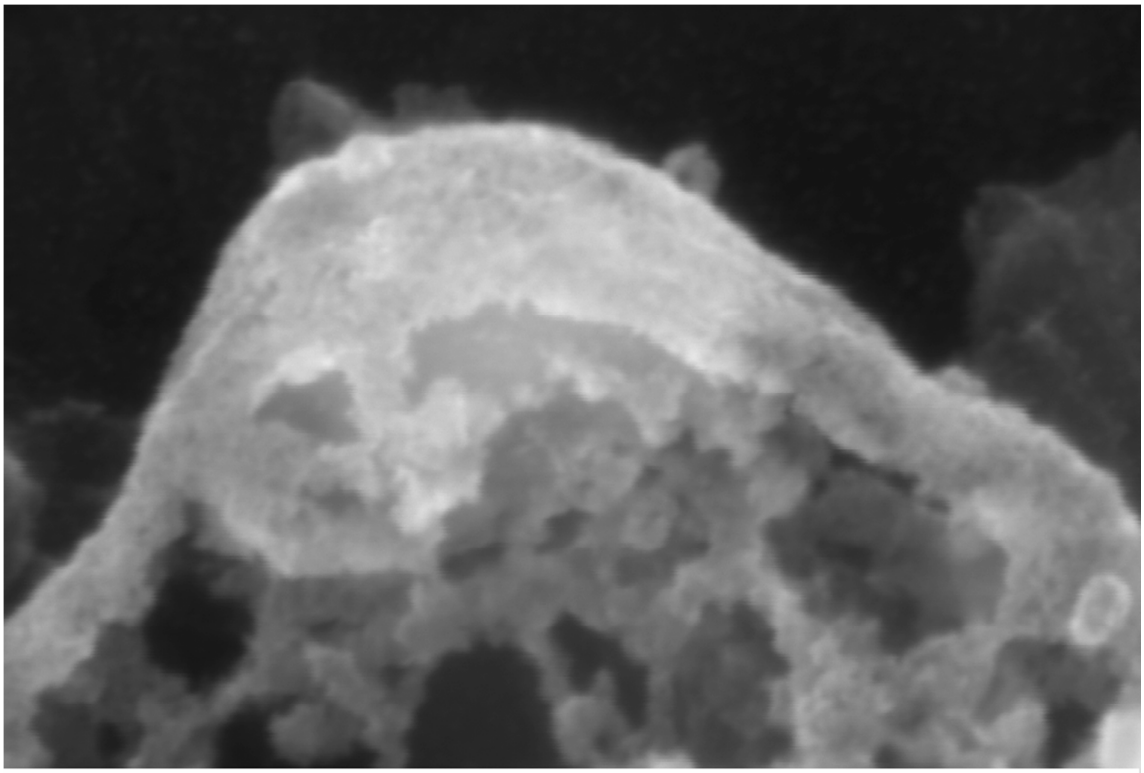


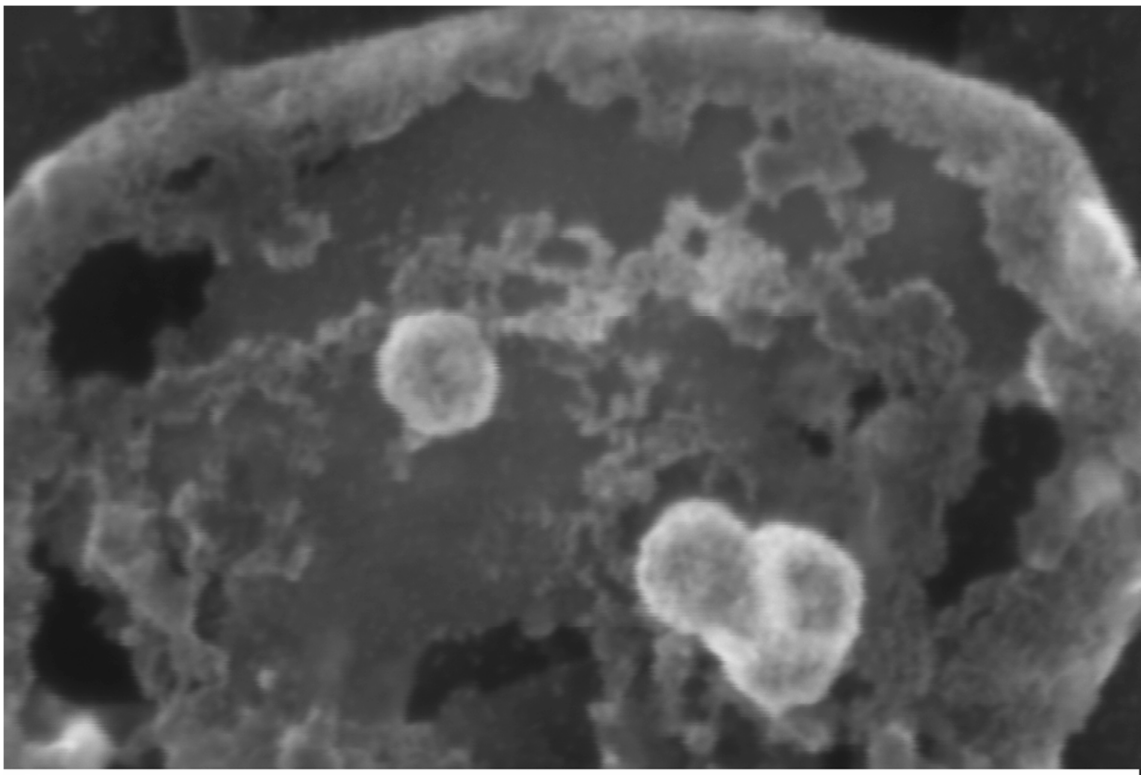

Figure S8: OER activity for Ru, el. RuO2 and th.$RuO_2$ measured in electrochemical flow cell: a) till 1.4 V, b) till 1.5 V and c) till 1.6 V.



20 nm

EHT = 7.00 kV Signal A = InLens Mix Signal = 0.1000 Chamber = 8.95e-004 Pa
WD = 6.1 mm Aperture Size = 30.00 µm File Name = Ru_011.tif

Date :27 Mar 2014



20 nm

EHT = 7.00 kV Signal A = InLens Mix Signal = 0.1000 Chamber = 1.04e-003 Pa
WD = 6.1 mm Aperture Size = 30.00 µm File Name = Ru_004.tif

Date :27 Mar 2014

Figure S9: Porosity formation in Ru sample after 2nd cycle from 0.05 to 1.6 V vs. RHE. Upper image is a close-up of Figure 3c. Lower one is a close-up of image S5c.


1. Mitsushima, S.; Uzuka, S.; Matsuzawa, K.; Ota, K.-i., Evaluation of Solubility of Ru in Acidic Solution. *Electrocatal* **2010**, *1*, 83-86.
2. Bratsch, S. G., Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K. *Journal of Physical and Chemical Reference Data* **1989**, *18*, 1-21.
3. Zeradjanin, A. R.; Topalov, A. A.; Van Overmeere, Q.; Cherevko, S.; Chen, X.; Ventosa, E.; Schuhmann, W.; Mayrhofer, K. J. J., Rational Design of the Electrode Morphology for Oxygen Evolution - Enhancing the Performance for Catalytic Water Oxidation. *RSC Advances* **2014**, *4*, 9579-9587.
4. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*; Pergamon Press: Oxford, New York, 1966, p 644 p.
5. Cherevko, S.; Zeradjanin, A. R.; Topalov, A. A.; Kulyk, N.; Katsounaros, I.; Mayrhofer, K. J. J., Dissolution of Noble Metals During Oxygen Evolution in Acidic Media. *ChemCatChem* **2014**, *6*, 2219-2223.