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# Engineering stable electrocatalysts by synergistic stabilization between carbide cores and Pt shells

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# Engineering stable electrocatalysts by synergistic stabilization between carbide cores and Pt shells

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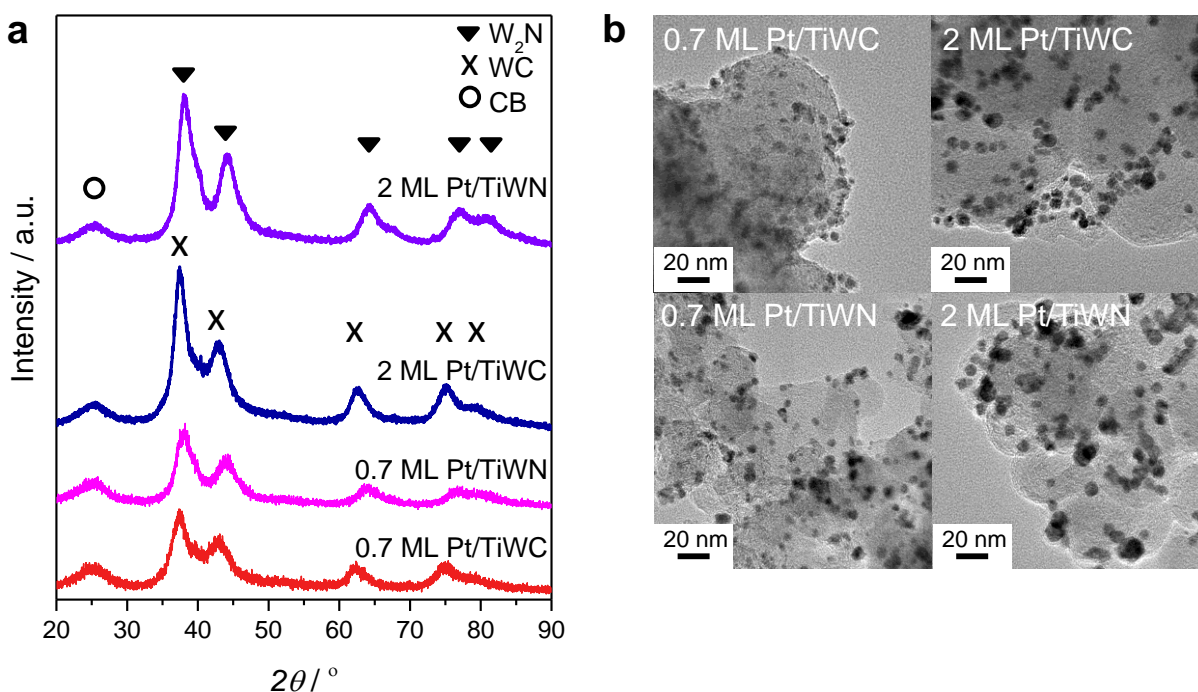
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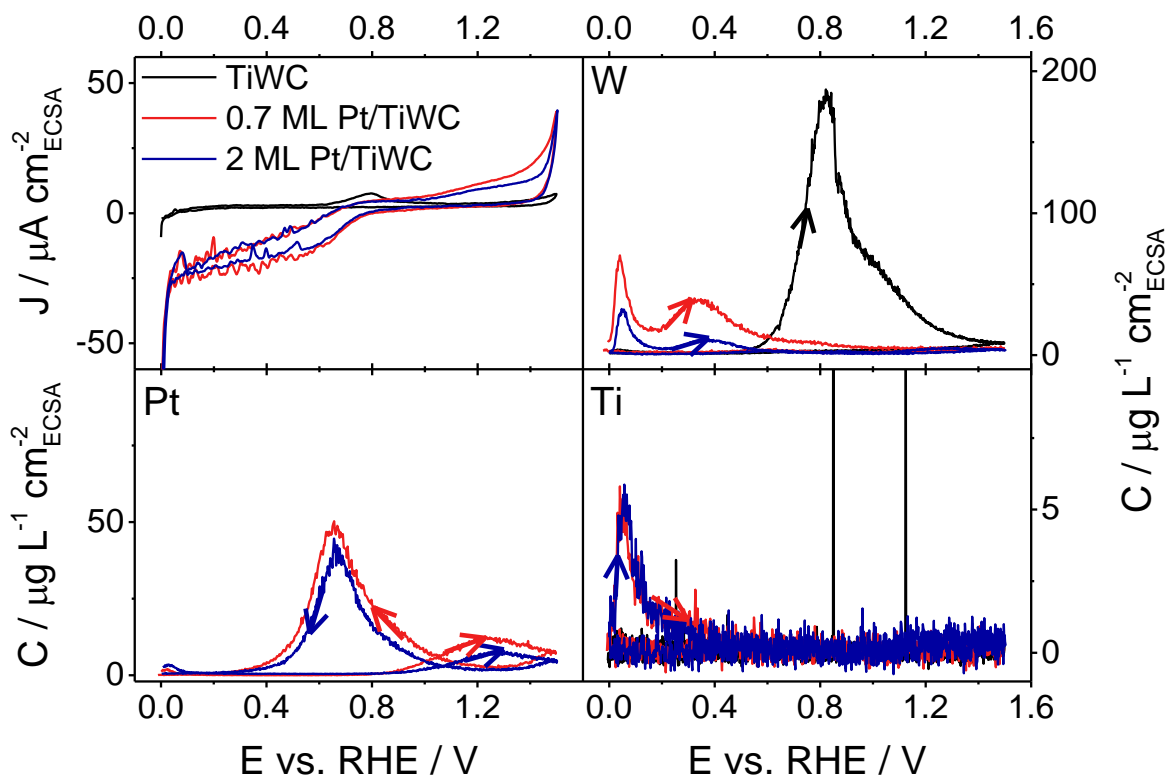
## Supplementary Information



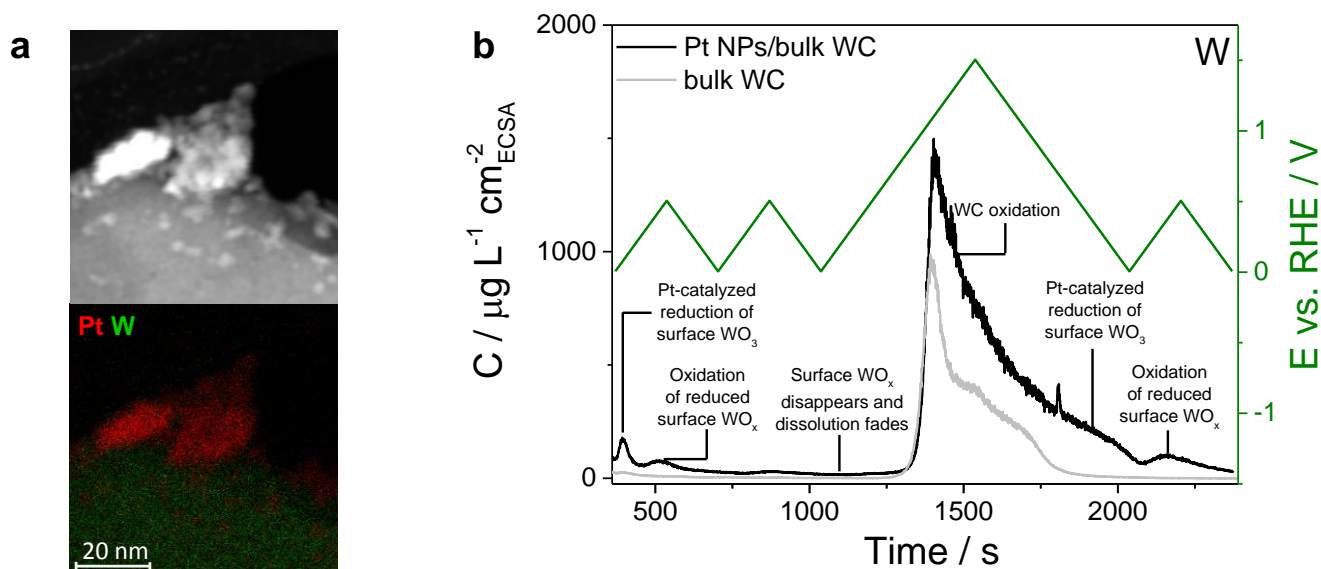
**Figure S1 a)** PXRD patterns and **b)** TEM images of core-shell materials.

**Table S1** Elemental compositions of core-shell materials as determined by ICP-MS.

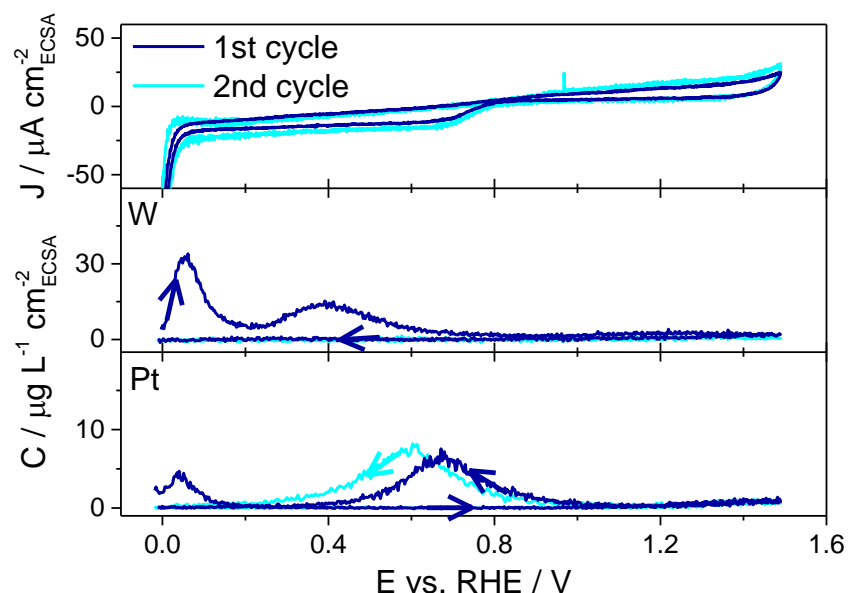
Material	Ti wt.% on C	W wt.% on C	Pt wt.% on C
0.7 ML Pt/TiWC and 0.7 ML Pt/TiWN	0.32	14.1	2.74
2 ML Pt/TiWC and 2 ML Pt/TiWN	0.63	22.6	6.29



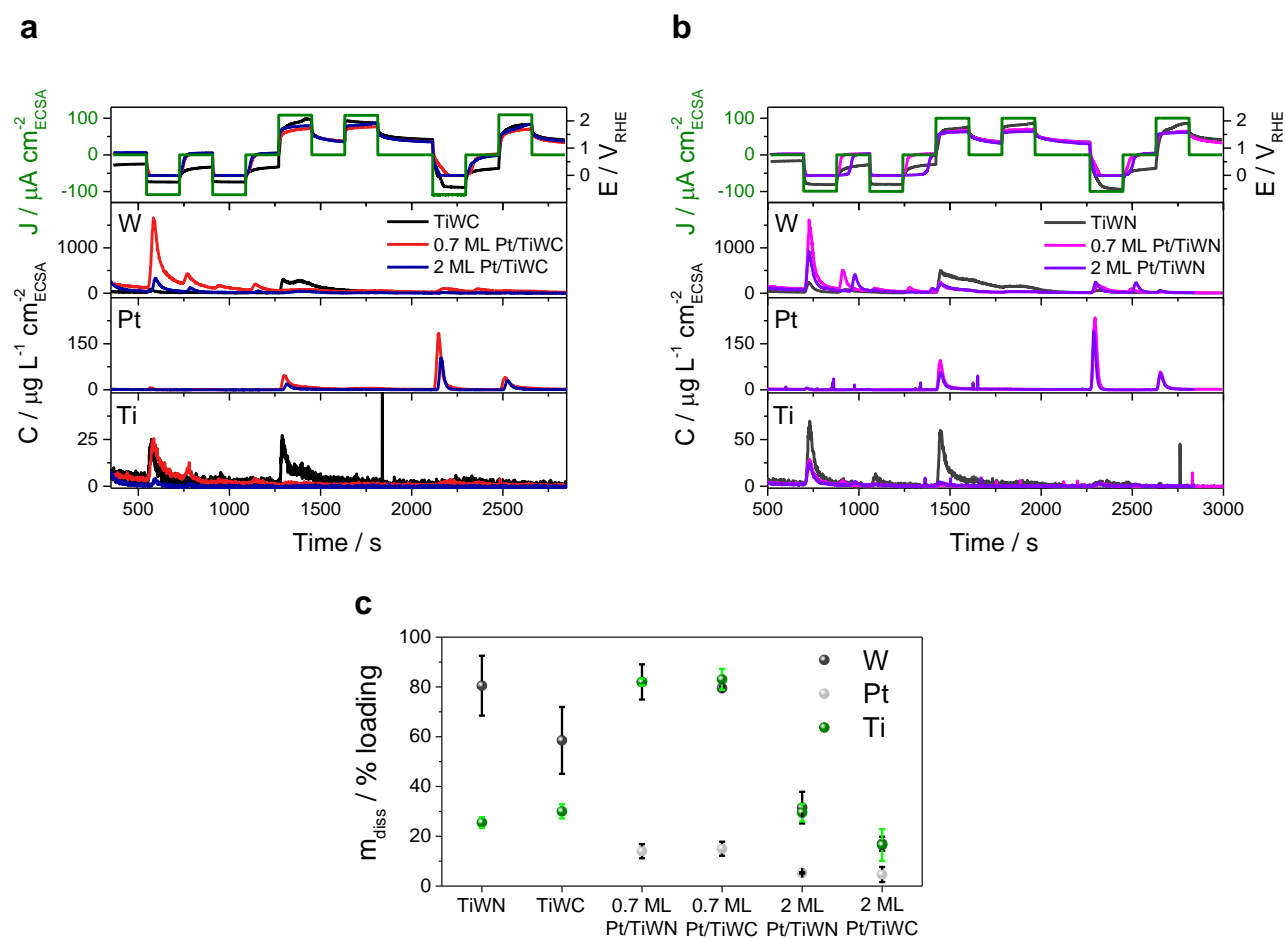
**Figure S2** First CV at  $2 \text{ mV s}^{-1}$  between  $0.0$  and  $1.5 \text{ V}_{\text{RHE}}$  in  $0.1 \text{ M HClO}_4$  and the corresponding dissolution profiles for carbide samples.



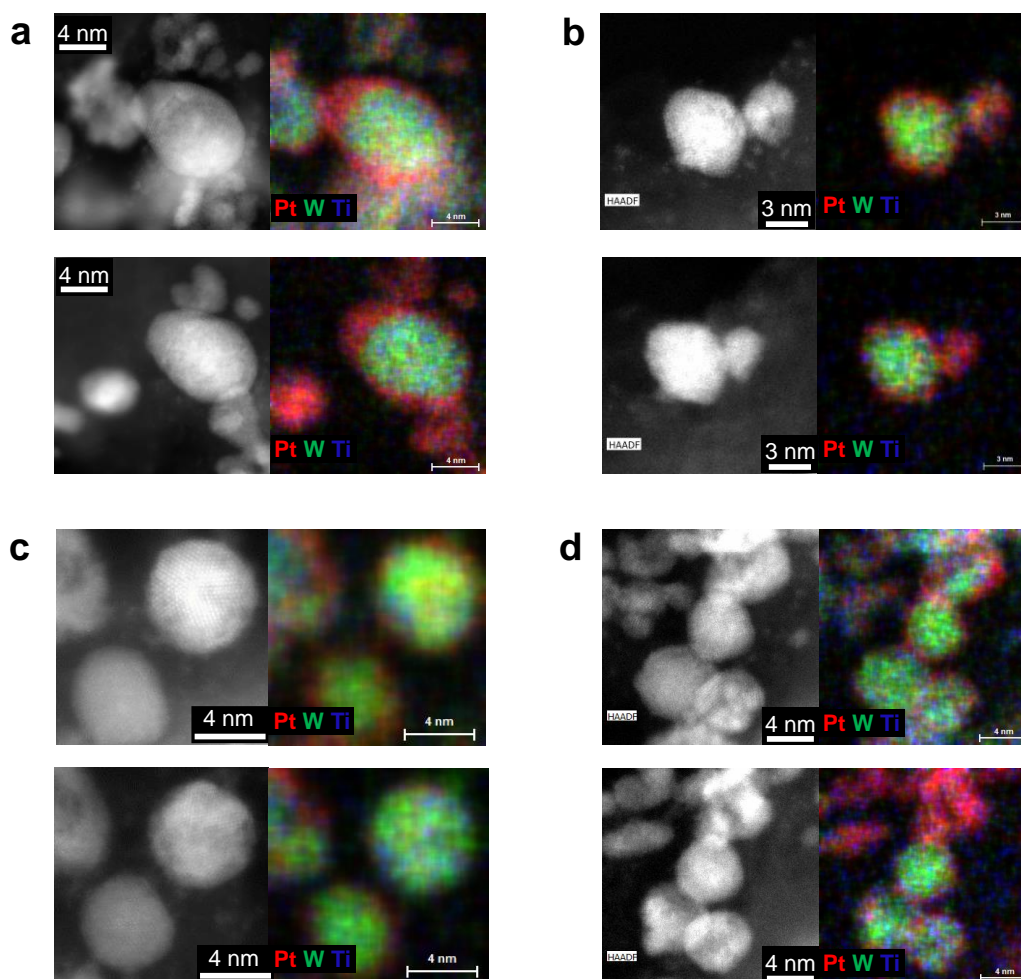
**Figure S3** a) STEM image and EDX elemental map of Pt NPs deposited onto bulk WC. b) Applied potential profile at  $2 \text{ mV s}^{-1}$  in  $0.1 \text{ M HClO}_4$  and the corresponding dissolution profile of W with time.



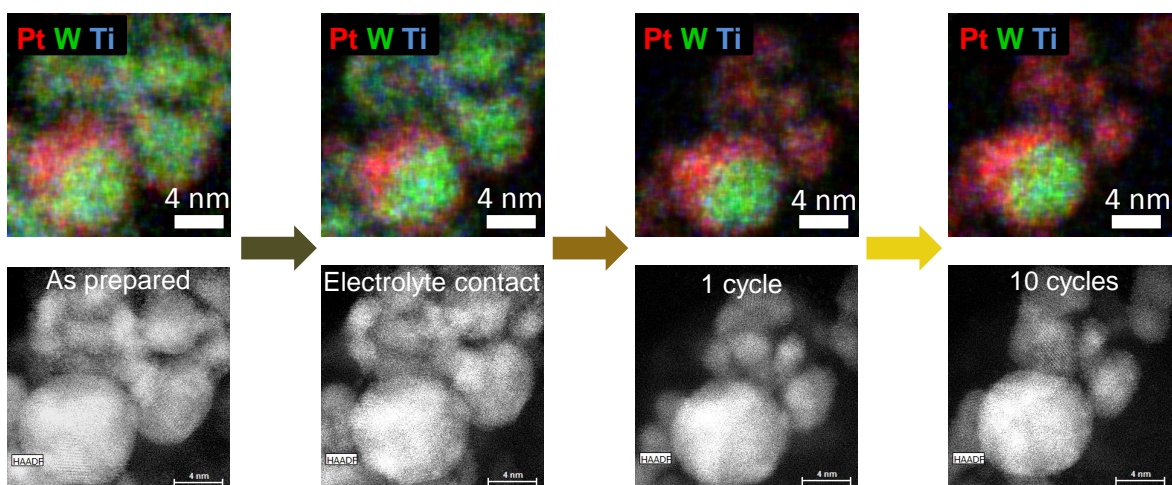
**Figure S4** Comparison of dissolution profiles between the first and second potential cycles for 2 ML Pt/TiWC.



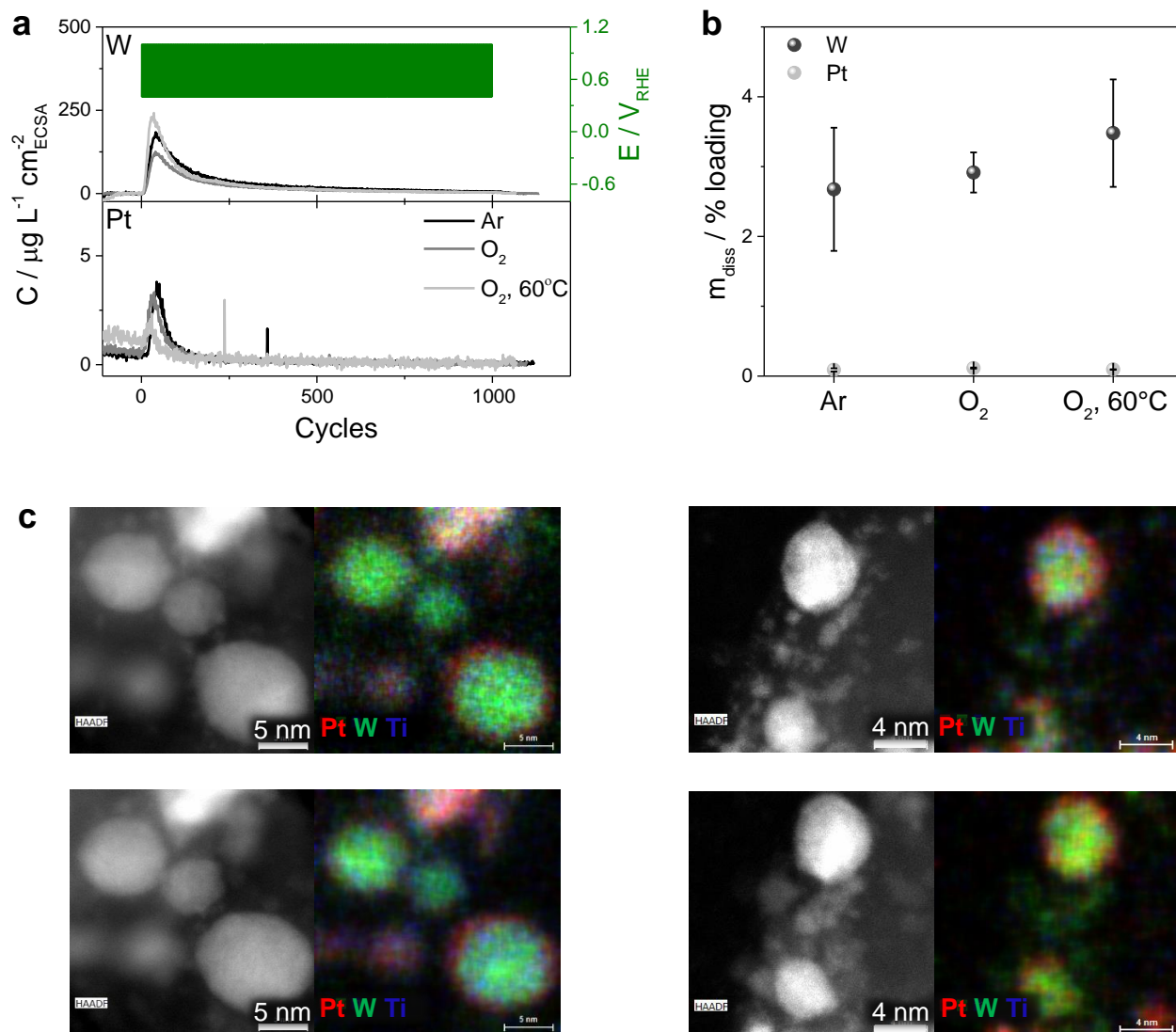
**Figure S5** Applied current density and resulting potential profiles in 0.1 M  $\text{HClO}_4$  along with corresponding dissolution profiles during SFC-ICP-MS galvanostatic measurements for **a)** carbides and **b)** nitrides. **c)** Total amount of metal dissolution during the galvanostatic measurements.



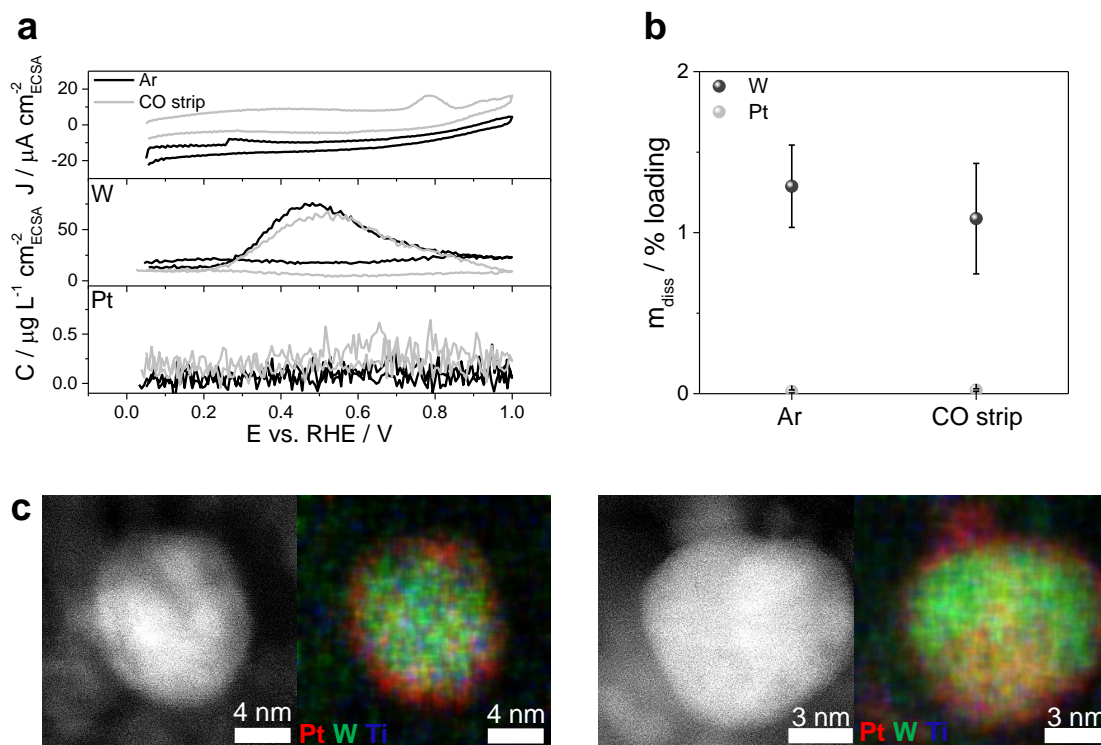
**Figure S6 a-d)** Identical location STEM images and corresponding EDX elemental maps of 2 ML Pt/TiWC before (upper panel) and after (lower panel) ASTs consisting of 10,800 cycles between 0.4 and 1.0  $V_{\text{RHE}}$  in Ar-sat 0.1 M  $\text{HClO}_4$  at a scan rate of  $1 \text{ V s}^{-1}$ .



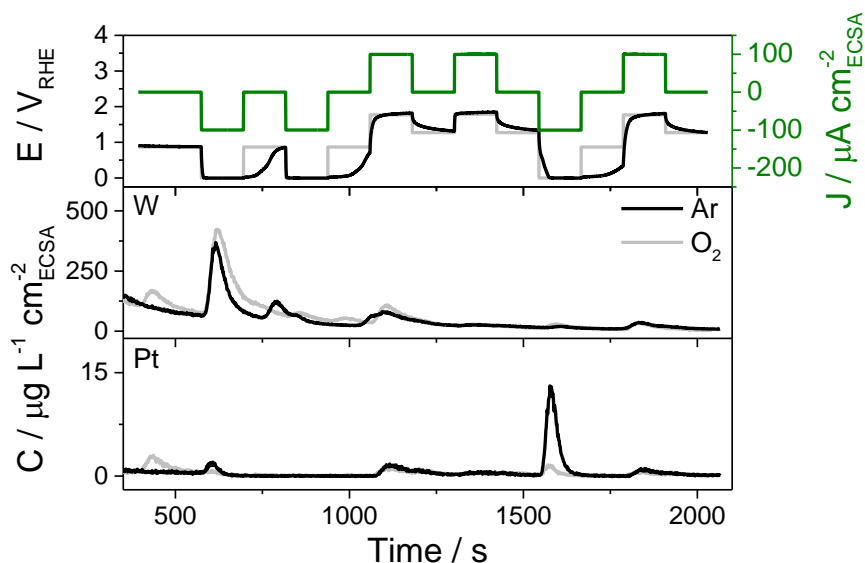
**Figure S7** Identical location STEM images and corresponding EDX elemental maps of 2 ML Pt/TiWC visualizing the degradation of particles at different stages: as prepared, after electrolyte contact, after 1 cycle, and after 10 cycles in 0.1 M  $\text{HClO}_4$ .



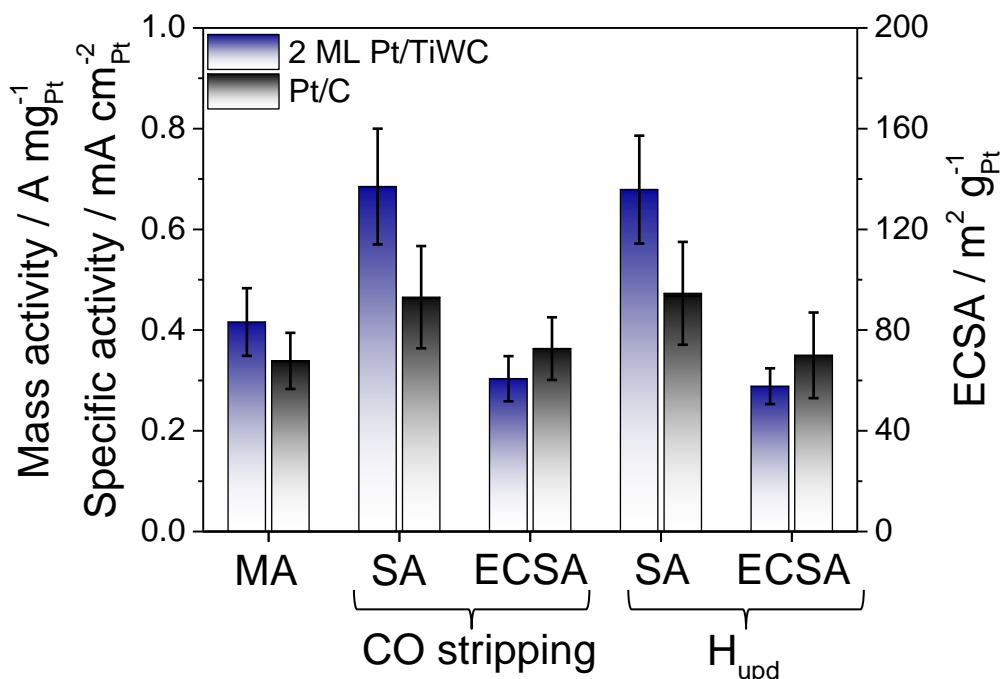
**Figure S8** **a)** W and Pt dissolution profiles of 2 ML Pt/TiWC during 1000 cycles between 0.4 and 1.0  $V_{\text{RHE}}$  at  $1 \text{ V s}^{-1}$  in Ar and  $\text{O}_2$ -sat 0.1 M  $\text{HClO}_4$  at room temperature and  $60^\circ\text{C}$ . **b)** Total dissolved amounts of W and Pt for experiments in **a**. **c)** Identical location STEM images and corresponding EDX elemental maps of 2 ML Pt/TiWC before (upper panel) and after (lower panel) ASTs consisting of 10,800 cycles between 0.4 and 1.0  $V_{\text{RHE}}$  at  $1 \text{ V s}^{-1}$  in air-sat 0.1 M  $\text{HClO}_4$ .



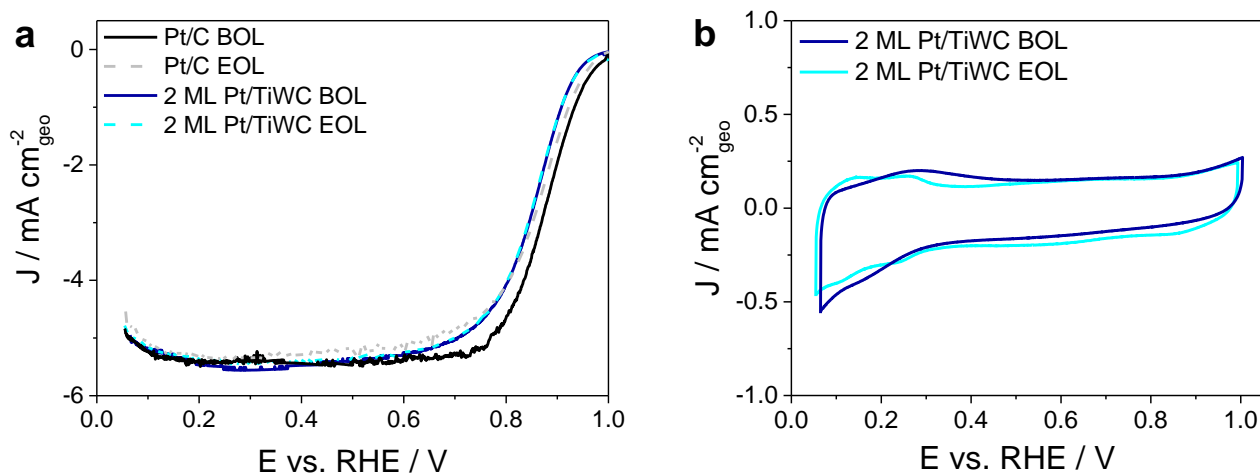
**Figure S9** a) CV of 2 ML Pt/TiWC from 0.05 to 1.0  $V_{\text{RHE}}$  at  $50 \text{ mV s}^{-1}$  in Ar-sat 0.1 M  $\text{HClO}_4$  and with pre-adsorbed CO at 0.05  $V_{\text{RHE}}$  for 7 min and corresponding W and Pt dissolution profiles. b) Total dissolved amounts of W and Pt for experiments in a. c) STEM images and corresponding EDX elemental maps of 2 ML Pt/TiWC after 10 consecutive CO stripping cycles.



**Figure S10** Applied current density profile, resulting potential profile, and W and Pt dissolution profiles for 2 ML Pt/TiWC in Ar-sat 0.1 M  $\text{HClO}_4$  during SFC-ICP-MS galvanostatic measurements. To compare with the case of  $\text{O}_2$ -sat electrolyte, potentiostatic steps mimicking the potential profile during the galvanostatic measurements in Ar-sat 0.1 M  $\text{HClO}_4$  were applied in  $\text{O}_2$ -sat 0.1 M  $\text{HClO}_4$ .



**Figure S11** Mass activities (MA) and specific activities (SA) at 0.9 V<sub>RHE</sub> and ECSAs calculated by CO stripping and H<sub>upd</sub> at beginning of life (BOL) in 0.1 M HClO<sub>4</sub>.



**Figure S12 a)** ORR polarization curves in O<sub>2</sub>-sat 0.1 M HClO<sub>4</sub> at 1600 rpm before (BOL) and after (EOL) ASTs consisting of 10,800 cycles between 0.4 and 1.0 V<sub>RHE</sub> in 0.1 M HClO<sub>4</sub> at a scan rate of 1 V s<sup>-1</sup>. Pt loading of 5 μg<sub>Pt</sub> cm<sup>-2</sup> for 2 ML Pt/TiWC and 20 μg<sub>Pt</sub> cm<sup>-2</sup> for Pt/C. **b)** CVs at 50 mV s<sup>-1</sup> in Ar-sat 0.1 M HClO<sub>4</sub> before and after ASTs.

### *Impact of NaOH pretreatment*

It has previously been shown that the surface of WC is covered with a labile oxide film which dissolves upon contacting the electrolyte in the SFC [1]. This contact peak creates a background signal which can impact the sensitivity of the ICP-MS during the measurement. If large particles with low specific surface area are used, the amount of dissolving oxide is low, so the background signal is relatively insignificant. However, for small nanoparticles with high surface area, the contact peak results in a high background concentration which declines very slowly. Most of these surface oxides can be removed by NaOH without influencing the electrochemistry [1]. Thus, we decided to use a 0.5 M NaOH pretreatment prior to the single potential cycle experiments in order to obtain the highest possible resolution for any electrochemical dissolution processes. In contrast, the galvanostatic experiments do not require the same potential dependent resolution as changes in electrochemical processes occur only when the applied current densities are altered for which the exact time spot is known. For this reason, no NaOH pretreatment was performed prior to the galvanostatic experiments, which allows for quantitative comparison as the initial metal loadings are known.

### **References**

- [1] Göhl, D. *et al.* Electrochemical stability of hexagonal tungsten carbide in the potential window of fuel cells and water electrolyzers investigated in a half-cell configuration. *Electrochim. Acta* **270**, 70-76 (2018).