Supporting information

Electrochemical Formation of Hydrous RuO$_2$ over Single Crystalline Ru(0001) Model Electrodes

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The EC cell design is based on the commercial EC cell (company ALS) and optimized to bring only the top surface of the single crystal in contact with the electrolyte solution (cf. figure S1). The cell is constructed of a copper sample holder with a notch for accommodating the single crystal; the electrical contact to the working electrode is realized by a gold wire which is spot welded to the bottom of the single crystal. A silicone mask covers the edges of the crystal in the sample holder to ensure that only the polished surface of the single crystal Ru(0001) is exposed to the electrolyte solution. The silicone bears a lining groove to accommodate the glass vial in a leak-proof way. The three electrode EC Cell consists of a gas inlet, a counter electrode, a reference electrode and the single crystal serving as working electrode.

**Figure S1**: a) Sample holder made from copper; b) the sample is immersed into a silicone polymer SF30 template so that only the Ru(0001) surface is exposed to the ultra-pure electrolyte solution; right) Assembly of the EC cell.
Figure S2: SEM und scanning tunneling microscopy (STM) image of the clean Ru(0001) surface. In SEM the in-lens detector was used. STM parameters: \( I=1 \) nA and bias voltage \( U=1V \). Details of the STM apparatus can be found in Ref. 1.

In Figure S3, we show the temperature evolution of the hydrous RuO\(_2\) layer in SEM for other regions on the surface of our sample. Most notably, with increasing annealing temperature the size of the observed islands grow in size. The dark regions disappear with increasing annealing temperature.
Figure S3: Temperature induced Island growth on the hydrous RuO$_2$ layer (Preparation: 1.32 V vs. SHE for 120s in 0.1M HClO$_4$) by annealing the sample under UHV conditions to predefined temperatures: 30°C: RT, 150°C, 300°C and 500 °C. The SEM images were recorded by the SE2 detector.

Table S1: O1s energy positions for various O-containing species used in the decomposition of O1s spectra on hydrous RuO2 as a function of the annealing temperature.

<table>
<thead>
<tr>
<th>Species</th>
<th>Binding energy/eV</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH-Ru(110)</td>
<td>O1s: 530</td>
<td>2</td>
</tr>
<tr>
<td>OH$_2$-Ru(110)</td>
<td>O1s: 532</td>
<td>2</td>
</tr>
<tr>
<td>RuO$_2$(110)</td>
<td>O1s: 529.5</td>
<td>3</td>
</tr>
<tr>
<td>CO$_2$ CO$_2$-$\delta$ adsorbed on metal surface</td>
<td>O1s: 532-535</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>C1s: 286-290</td>
<td>4</td>
</tr>
<tr>
<td>OH-Ru(0001)</td>
<td>O1s: 531-531.7</td>
<td>5</td>
</tr>
<tr>
<td>OH$_2$-Ru(0001)</td>
<td>O1s: 533.2</td>
<td>5</td>
</tr>
<tr>
<td>O-Ru(0001)</td>
<td>O1s: 530</td>
<td>3</td>
</tr>
</tbody>
</table>
**Figure S4:** Evaluation of the O1s XPS spectra of carbon-contaminated hydrous RuO$_2$ layer (prepared by polarizing at 1.35 V for 300 s in 0.1M HClO$_4$) as a function of the annealing temperature. Carbon contamination due to storing the sample in ambient atmosphere for 12h.
Figure S5: a) O1s XPS spectra of carbon-contaminated hydrous RuO$_2$ layer (prepared by polarizing at 1.32V for 120s in 0.1M HClO$_4$) as a function of the annealing temperature. Carbon contamination due to storing the sample in ambient atmosphere for 12h. b) Ru3d XPS spectra of the same hydrous RuO$_2$ layer as a function of the annealing temperature. These XPS spectra were recorded in our STM chamber$^1$ equipped with XPS; please note that here the resolution is worse than for the measurements with the PHI Versaprobe. c) ratios of the integrated intensity of Rud$_{5/3}$ and Ru3d$_{3/2}$. 
Figure S6: Evaluation of the XPS data O1s XPS spectra of the hydrous RuO$_2$ layer (prepared by polarizing at 1.37 V for 300 s in 0.1M HClO$_4$, nominal no carbon contamination) as a function of the annealing temperature.
Figure S7: Particles formed on the hydrous RuO$_2$ surface (prepared by polarizing at 1.32 V for 120s in 0.1M HClO$_4$) by annealing the sample to 600°C. Blue: rectangular shaped particles; Purple: hexagonal particles, and Green: triangular particles.
Figure S8: RHEED patterns of hydrous RuO$_2$ layer on Ru(0001) after annealing to various temperatures in UHV. Besides the substrate (strong reflections) also reflections from RuO$_2$ in (100) orientation (positions are indicated by red circles).

References