Supporting Information

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Electrochemical Hydrogen Storage in Amine-Activated Polydopamine

Halime Coskun, Abdalaziz Aljabour, Theresia Greunz, Matthias Kehrer, David Stifter, and Philipp Stadler*
Supplementary Information

Halime Coskun  Abdalaziz Aljabour  Theresia Greunz  Matthias Kehrer  David Stifter  Philipp Stadler

Dr. Halime Coskun, Dr. Abdalaziz Aljabour, Dr. P. Stadler
Institute of Physical Chemistry, Johannes Kepler University Linz, Altenberger Strasse 69, 4040 Linz, Austria

Dr. Theresia Greunz, Matthias Kehrer, Prof. David Stifter
Center for Surface and Nanoanalytics, Johannes Kepler University Linz, Altenbergerstrasse 69, 4040 Linz, Austria

Dr. P. Stadler
Linz Institute of Technology (LIT), Johannes Kepler University Linz, Altenbergerstr. 69, A-4040 Linz, Austria Email Address: philipp.stadler@jku.at

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Supplemental Information contains following additional figures:

1. Figure S1: Reaction kinetics (chronocoulometry) at maximum ab- and desorption peak: reaction constants.
2. Figure S2: Noise limit of electrochemical-induced absorption (in-situ FTIR) spectroelectrochemical detection of vibronic differential spectra vs. applied bias.
3. Figure S3: Electrochemical impedance spectroscopy (EIS) to measure the cell-constant.
4. Table S1: summarized electrochemical cell constants.
5. Figure S4: X-ray photoelectron spectroscopy - S2p high-resolution scans of amine-activated polydopamine (aaPDA).
6. Figure S5: X-ray photoelectron spectroscopy - C1s high-resolution scans of aaPDA.
7. Figure S6: X-ray photoelectron spectroscopy - survey scan of aaPDA.
8. Figure S7: SEM pictures of as-deposited aaPDA.
9. Figure S8: X-ray photoelectron spectroscopy - N1s and S2p high resolution scans of as-deposited, before- (dipped in electrolyte) and after-electrosorption.
10. Figure S9: X-ray photoelectron spectroscopy - F1s high resolution scans of as-deposited, before- (dipped in electrolyte) and after-electrosorption.
11. Figure S10: SEM pictures of aaPDA as-deposited and after electrosorption
12. Figure S11: Alternative electrolyte: Hydrogen electrosorption in 1 M HCl.
13. Figure S12: Influence of slower scan rate (5 mV s$^{-1}$) on the electrosorption (peak broadening).
Figure 1: **Charge kinetics**: (top) Absorption: linear fit of the chronocoulometry over (integrated) time with the reaction constant $k_{\text{red}} = 0.034 \text{ s}^{-1}$. (bottom) Desorption: linear fit, $k_{\text{ox}} = 0.018 \text{ s}^{-1}$ (corresponding to 30 and 56 s, respectively).
Figure 2: Detection limit of electrochemical-induced absorption (EIA): Noise level of reference minimum current scan, corresponding to +0.2 V vs. RHE, isosbestic point, at $10^{-4} \Delta T/T$. 

Figure 2 shows the detection limit of electrochemical-induced absorption (EIA). The noise level of the reference minimum current scan, corresponding to +0.2 V vs. RHE, is depicted at an isosbestic point, indicated by the isosbestic point at $10^{-4} \Delta T/T$. The graph illustrates 100 repeats at +0.2 V vs. RHE, with the noise level marked by the dots on the graph.
Figure 3: Electrochemical impedance spectroscopy: Cell constants measured by the impedance in 1 M trifluoromethanesulfonic acid (pH = 0), between Pt-Pt, Pt-carbon felt (CF) and Pt - Carbon Felt + aaPDA. The corresponding cell parameters are summarized in Table S1.
Table 1: Cell constants of electrosorption cell measured by electrochemical impedance spectroscopy.

<table>
<thead>
<tr>
<th>WE</th>
<th>CE</th>
<th>$R_{sol.} / \Omega$</th>
<th>$R_{WE} / k\Omega$</th>
<th>$R_{membrane} / \Omega$</th>
<th>C / F</th>
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<tbody>
<tr>
<td>Pt</td>
<td>Pt</td>
<td>1.8</td>
<td>18.3</td>
<td>34</td>
<td>-</td>
</tr>
<tr>
<td>Pt</td>
<td>CF</td>
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<td>1013</td>
<td>34</td>
<td>-</td>
</tr>
<tr>
<td>Pt</td>
<td>CF-aaPDA</td>
<td>2.2</td>
<td>4.2</td>
<td>34</td>
<td>0.0534</td>
</tr>
</tbody>
</table>

Figure 4: **X-ray photoelectron spectroscopy**: S2p high resolution spectra of aaPDA (on carbon felt) show the composition of sulfur to relate to bisulfate moieties.
Figure 5: X-ray photoelectron spectroscopy: C1s high resolution scans of aaPDA (on carbon felt) show the composition of carbon to relate mainly to C-C bonding, functional sites (C-O, C-N) and sp² ($\pi - \pi^*$) carbon.
Figure 6: **X-ray photoelectron spectroscopy**: Survey scan of aaPDA on carbon felt. Elements on the CVD-grown aaPDA are C, N, O and S.

Figure 7: **aaPDA structure**: Scanning electron microscopy pictures of aaPDA.
Figure 8: aaPDA structure as-synthesized, before (dipped) and after electrolysis: constant N1s (indicating similar aaPDA), while anion exchange from (bi)sulfate to triflate (TfO\(^-\)) is observed.

Figure 9: aaPDA structure as-synthesized, before (dipped) and after electrolysis: rise of the F1s peak.
Figure 10: Scanning electron microscopy (SEM) before and after electrosorption: structure remains almost unchanged, except for a gradual exchange of anions (sulfate to TfO\(^-\), dissolution of excess sulfuric acid from the synthesis).
Figure 11: aaPDA electrosorption in 1 M HCl: degradation of the sorption peaks after a few cycles.
Figure 12: CVs at 5 mV s\(^{-1}\) scan rate: Broadening of the electrosorption peak by the lower scan rate.