Metal-Organic-Frameworks on 3D-Printed Electrodes:
In-Situ Electrochemical Transformation towards
Oxygen Evolution Reaction

Yulong Ying, ‡a Michelle Philippa Browne ‡a and Martin Pumera *ab

a Center for Advanced Functional Nanorobots, Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic

b Central European Institute of Technology, Brno University of Technology, Future Energy and Innovation Laboratory, Purkyňova 656/123, Brno, CZ-616 00, Czech Republic

E-mail: pumera.research@gmail.com

Supporting Information
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**Figure S1** Digital images of (a) Bare 3D-printed Ti Electrode, (b) ZIF-67/Ti Electrode, and (c) Activated ZIF-67/Ti-E Electrode.

**Figure S2** XRD characterization of the 3D-printed Ti electrode (1#), ZIF-67/Ti electrode (2#), ZIF-67/Ti-E electrode (3#), ZIF-67/Ti-C electrode (4#), and ZIF-67/Ti-E+C electrode (5#).

**Figure S3** SEM characterization of the ZIF-67/Ti electrode.

**Figure S4** XPS survey and high-resolution XPS spectra of Co 2p\textsubscript{2/3} for different electrodes.

**Figure S5** SEM characterizations of the electrode during the electrochemical transformation process with (a) 5\textsuperscript{th} and (b) 10\textsuperscript{th} CV cycling.

**Figure S6** O1s XPS characterizations of the (a) ZIF-67/Ti-E electrode (3#), (b) ZIF-67/Ti-C electrode (4#), and (c) ZIF-67/Ti-E+C electrode (5#).

**Figure S7** SEM image of ZIF-67 powders.

**Figure S8** EIS plots.

**Table S1.** OER literature review of MOF-based and Co-based oxides on various supports in 1.0 M NaOH electrolyte.
Figure S1 Digital images of (a) Bare 3D-printed Ti Electrode, (b) ZIF-67/Ti Electrode, and (c) Activated ZIF-67/Ti-E Electrode.

The digital images clearly show the coverage by the ZIF-67 and electrochemical transformation process on the surface of the 3D-printed Ti electrode. Bare 3D-printed Ti electrode has a silver color in Fig. S1a. After the coating with ZIF-67, the surface turns to purple in Fig. S1b. The electrochemical transformation process results in the black surface due to the production of cobalt-based oxides.
The XRD confirms that the 3D-printed Ti electrode consists of Ti and Al (The commercial material used to make the Ti based supports in this study is Ti-6Al-4V) and that the ZIF-67 deposition on the surface of the electrode was successful. The disappearance of the ZIF-67-related diffraction peaks indicates the transformation of the ZIF structure to the amorphous cobalt. There are no additional XRD peaks for the ZIF-67/Ti-E electrode (3#), ZIF-67/Ti-C electrode (4#), and ZIF-67/Ti-E+C electrode (5#) visible in the respective diffractograms. No change in the diffraction pattern of the 3D-printed Ti electrode was observed during the experiment, indicating the chemical and physical stability of the composite.
Figure S3 SEM characterization of the ZIF-67/Ti electrode.

Figure S4 XPS survey and high-resolution XPS spectra of Co 2p$_{2/3}$ for different electrodes.

There are only two fitted peaks in the Co 2p$_{2/3}$ XPS region at a binding energy of 781.6 eV and 786.6 eV present in the spectrum of the ZIF-67/Ti electrode, which are attributed to Co 2p$_{2/3}$ main peak and a satellite peak. After electrochemical transformation process for the ZIF-67/Ti-E electrode the Co 2p$_{2/3}$ region can be fitted to a Co$^{2+/3+}$ (Co$_3$O$_4$) multiplet set with a minor contribution to another cobalt oxide.$^1$ The Co 2p$_{2/3}$ XPS region for the ZIF-67/Ti-C electrode and ZIF-67/Ti-E+C electrode with calcination treatment can all be contributed to Co$^{2+/3+}$ (Co$_3$O$_4$).$^1$
Figure S5 SEM characterizations of the electrode during the electrochemical transformation process with (a) 5th and (b) 10th CV cycling.

Figure S6 O1s XPS characterizations of the (a) ZIF-67/Ti-E electrode (3#), (b) ZIF-67/Ti-C electrode (4#), and (c) ZIF-67/Ti-E+C electrode (5#).

As shown in Fig. S6, it is indicated that the ZIF-67/Ti-C electrode (4#) and (c) ZIF-67/Ti-E+C electrode (5#) have a similar O1s peak, three peaks were observed at binding energies around 530 eV, 531 eV, and 532 eV, which are associated to Co$_3$O$_4$ according to Biesinger and co-workers.\textsuperscript{1} While the ZIF-67/Ti-E electrode has a more complicated O1s peak pattern at binding energies around 529 eV, 530 eV, 533 eV, and 535 eV. We suggested that this higher binding energy shift is attributed to the presence of Co(IV) in the system during the electrochemical transformation process. While the three lower binding energies are associated to Co$_3$O$_4$ similar to the ZIF-67/Ti-C electrode (4#) and (c) ZIF-67/Ti-E+C electrode (5#).
**Figure S7** SEM image of ZIF-67 powders.

**Figure S8** EIS plots.
Table S1. OER literature review of MOF-based and Co-based oxides on various supports in 1.0 M NaOH electrolyte.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Substrate (Area cm²)</th>
<th>Overpotential (mV) at 10 mA cm⁻²</th>
<th>Tafel plot (mV dec⁻¹)</th>
<th>TOF (s⁻¹)</th>
<th>Ref.</th>
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<tr>
<td>1</td>
<td>CoO₂ₓ/CoO₄</td>
<td>Ti 3D-printed electrode (6.3 cm²)</td>
<td>360</td>
<td>52</td>
<td>6.1</td>
<td>This work</td>
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<td>Commercial IrO₂</td>
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<td>Yolk@shell CoO₂/HNCP-40</td>
<td>Glassy carbon electrode (0.196 cm²)</td>
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<td>69</td>
<td>0.033</td>
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<td>Co₃O₄/C-MWCNTs</td>
<td>Glassy carbon electrode (0.071 cm²)</td>
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<td>n/a</td>
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<td>Co-CNT/PC</td>
<td>Ni foam (1 cm²)</td>
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<td>C-MOF-C₇-900</td>
<td>Glassy carbon rotating disk (0.196 cm²)</td>
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<td>FeNi@N-CNT</td>
<td>Ni foams</td>
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<td>47.7</td>
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References:


