

## Supplementary information

# Ion-solvating membranes as a new approach towards high rate alkaline electrolyzers

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## Experimental details

**Membrane preparation.** The *m*-PBI polymer (inherent viscosity 1.9 dL g<sup>-1</sup> measured at 30.0°C in an Ubbelohde viscometer, 96% H<sub>2</sub>SO<sub>4</sub> with 500 mg dL<sup>-1</sup> solid content) was synthesized in-house according to common procedures, as described elsewhere<sup>1</sup>. The polymer was cast from a *N,N*-dimethylacetamide solution (4.6% solid content) in petri dishes to form membranes of dry thicknesses of 20 and 40 μm. After careful washing in demineralized water at 90°C for at least 4 h, the membranes were doped at room temperature at least overnight prior to cell assembly by submersion in 24 wt% KOH (aq), resulting in approximately a doubling of thickness due to swelling, yielding membrane thicknesses of approximately 40 and 80 μm. Zirfon PERL (500 μm) was supplied by Agfa.

**Electrode preparation.** Perforated nickel plates were supplied by Veco B.V. with a thickness of 340 μm, a void fraction of 60% and a hole diameter of 1.2 mm. Uncoated perforated plate electrodes were welded to the nickel flowfield plates when used as anodes. The Raney nickel electrodes used in this study were fabricated by means of vacuum plasma spraying (VPS). The procedure has been described in detail in previous publications<sup>2-4</sup>. For the cathode coatings (hydrogen evolution) gas-atomized Ni-Al-Mo alloy powder containing 39 wt% Ni, 44 wt% Al, and 17 wt% Mo (H.C. Starck, Germany) with a particle size below 40 μm was used. The anode coatings were prepared from a Ni-Al alloy powder composed of 56 wt% Ni and 44 wt% Al. The powders were plasma sprayed onto 340 μm thick perforated Ni sheets. The thermal spray parameters were: 25 kW torch power (430 A, 57 V), 45 SLPM (standard liters per minute) Ar, 4 SLPM H<sub>2</sub> and 10 SLPM He as plasma gases, 70 mbar tank pressure and 200 mm spraying distance. Prior to coating, the Ni sheets were grit-blasted and chemically etched using a 34% HCl solution. The layer thickness was in the range of 110-130 μm. Activation of the Raney Ni electrodes was performed in 24 wt% KOH with 100 g L<sup>-1</sup> sodium-tartrate dihydrate to complex the leached out aluminium hydroxides and prevent precipitation of aluminium hydroxides. About 50-100 cm<sup>2</sup> (2-4 electrodes) were activated per half-liter of solution. The solution was heated to 80°C, and the electrodes were submerged for 24 hours, after which they were removed, rinsed and stored in water to prevent pyrophoric re-oxidation.

**Cell test and electrochemical characterization.** Square-shaped 5 cm × 5 cm electrodes were assembled horizontally with the separators in a zero gap configuration using Ni bipolar plates and polytetrafluoroethylene (PTFE) gaskets. The flowfield design was a pin-type. The cells were operated vertically and 24 wt% KOH electrolyte was circulated in two partially separated circuits with 50 ml min<sup>-1</sup> by PTFE diaphragm pumps. The KOH (aq) was prepared from KOH pellets (assay >85%) and MiliQ water, but was otherwise used as-prepared without any purification. Two 1.5 L storage tanks were connected by a narrow tube in the bottom to equilibrate the electrolyte levels. Heating was performed in a pre-heating cell, as well as in the test cell, and the temperature was increased to 80°C prior to starting the cell.

A typical cell test was initiated by a 12 hour break-in at 40 mA cm<sup>-2</sup> followed by a step-wise galvanostatically-recorded polarization curve with 5 minutes per current density point, up to either a limit of 2.8 V or 4 A cm<sup>-2</sup>. Galvanostatic electrochemical impedance spectroscopy (GEIS) was recorded at several current steps in a separate polarization curve immediately following the primary polarization curve. The impedance response was recorded in the frequency range of 100 kHz-1 Hz with an amplitude corresponding to 10% of the current density setpoint, however due to instrument limitations on the high current range impedance recorded above 25 kHz yielded null-values and was therefore disregarded. The cells were kept for 1-2 minutes at each current density step prior to recording the impedance measurements. The electrochemical data were recorded with a Biologic HCP 1005 potentiostat. For the long-term tests a Conradi Electronic GmbH power supply was used and manually set, alternatingly, to 100 or 1000 mA cm<sup>-2</sup>, while the cell potential was monitored with a Biologic HCP1001 potentiostat. Water was regularly supplied to keep the electrolyte concentration constant. For long-term tests, the anode gas was passed through a bubble flask and drying steps with silica gel and molecular sieves, after which the H<sub>2</sub> in O<sub>2</sub> level was monitored with a flame ionization detector (FID). Gas was occasionally sampled for gas chromatography analysis, which revealed good correspondence with the FID values. The included crossover values were recorded prior to changing current density setpoint during long-term tests, corresponding to approximately 16 h of equilibration at 100 mA cm<sup>-2</sup>, and 8 h at 1000 mA cm<sup>-2</sup>. The hydrogen crossover flux  $\Phi$  was calculated from the gas-phase hydrogen concentration assuming that no recombination was taking place and 100% faradaic efficiency towards oxygen evolution. The specific permeability  $\varepsilon$  was then calculated on basis of the initial membrane thickness  $d$  and the hydrogen partial pressure at the cathode  $p_{H_2}$ .

$$\varepsilon = \Phi \frac{d}{p_{H_2}}$$

The single 0.00% measurement was not considered when calculating the specific permeability range, and the calculated lower end of the range correspond to 0.01% at 1000 mA cm<sup>-2</sup>.

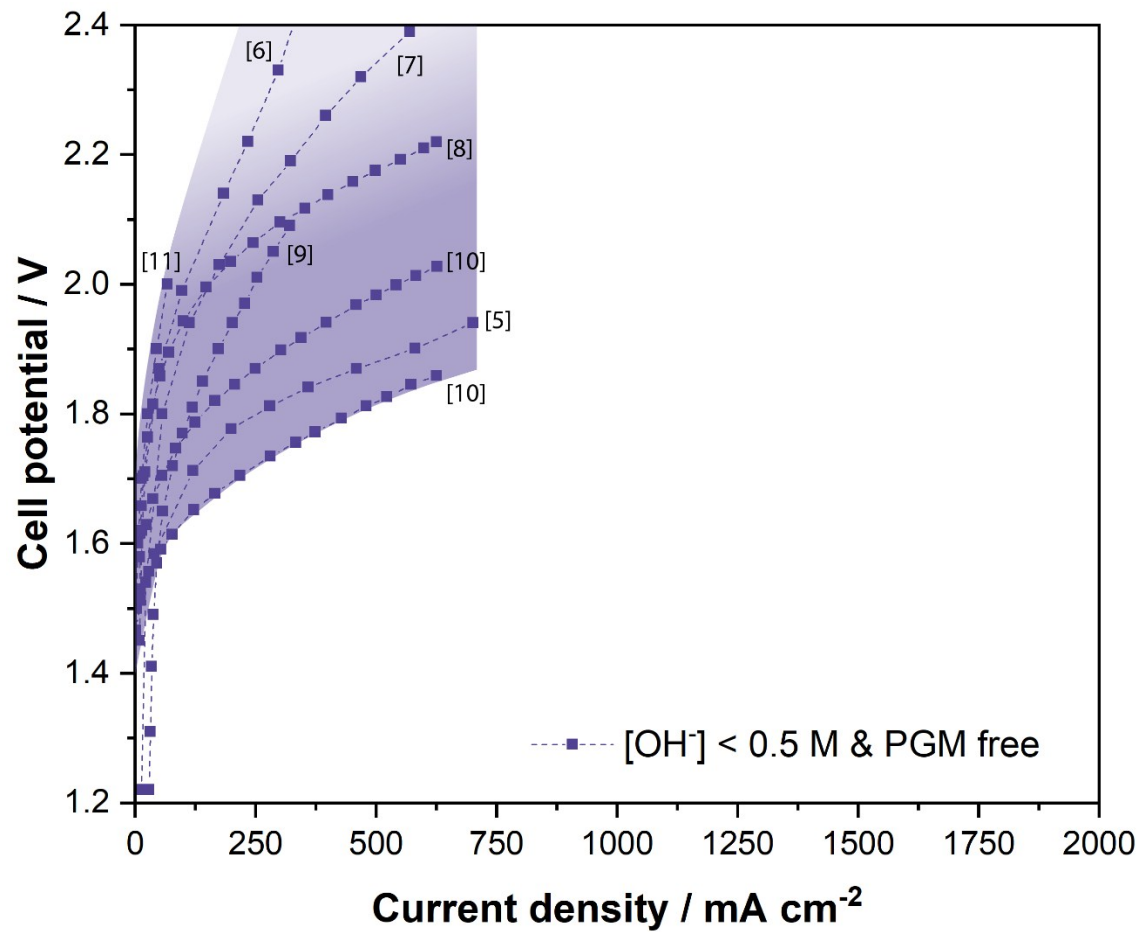
### **Published alkaline membrane-based electrolyzer data**

Figure 2 was prepared by outlining the boundary obtained by plotting extracted datasets for each category. The upper boundary from each category has been omitted in the graph for clarity and there is in principle no upper boundary with regard to poor polarization performance. What is interesting is the high performance region, and the capability for high current density. Data used to compile the different regions were by default the best performing polarization curve presented in the respective publications. Consequently, if several temperatures were evaluated, generally only the highest temperature dataset is included. The individual categories are outlined with the datasets they are based on in Figure S1 to S4, with specific cell details for the different references available in Table S1 to S4. The data points shown with markers were obtained by extracting values from published graphs, as opposed to obtaining the primary data from the authors. Hence, depending on the data clutter and graphical presentation in the original figure, the markers in Figure S1 to S4 do not correspond exactly one-to-one to every marker in the original publications. For instance, in cases where data was extracted from line-graphs or if the inclusion of every original point would needlessly clutter there herein shown graphs.

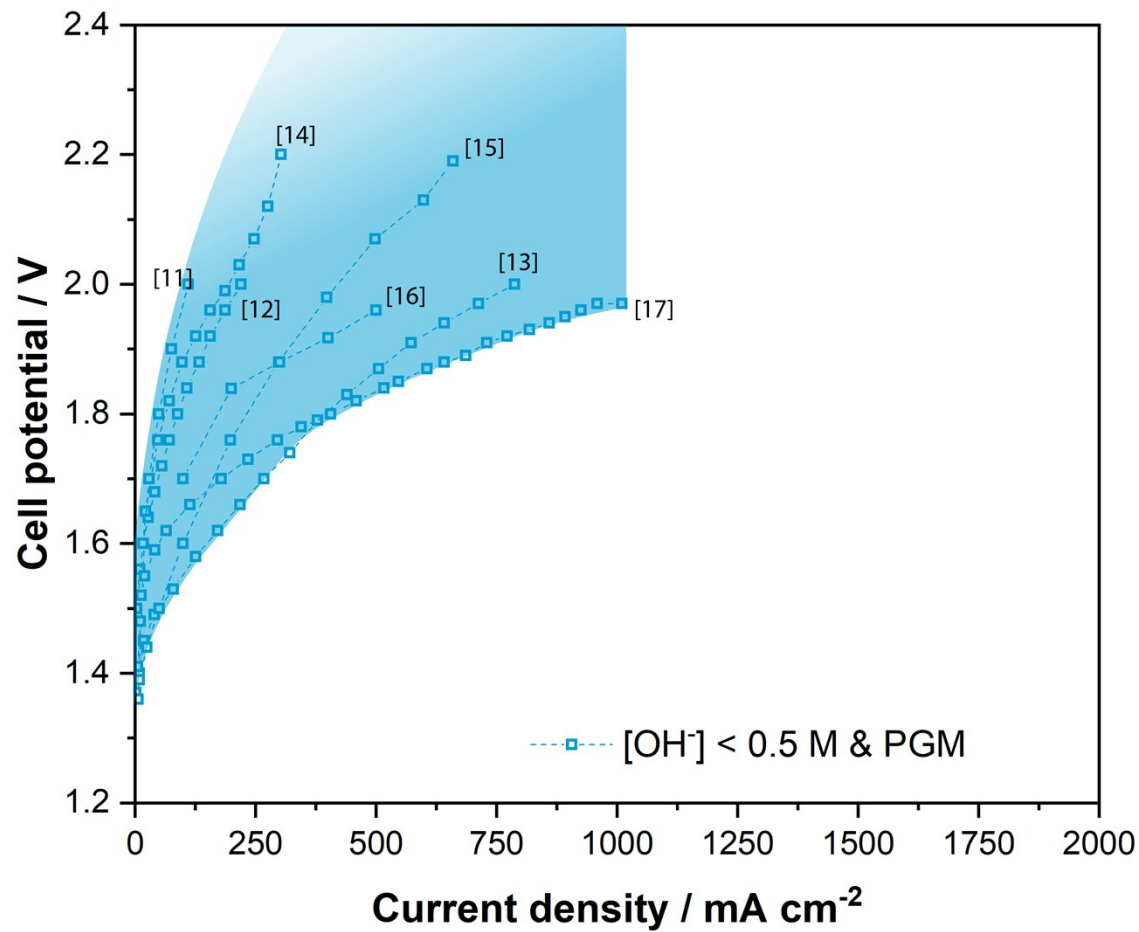
For Table S1 to S4 the following abbreviations are used, but the reader is encouraged to seek out the original reference for a more detailed description of e.g. the membrane or cell components.

- AB-PBI = poly(2,5-benzimidazole)
- ANEX = anion exchange particles
- BMA = butyl methacrylate
- CC = carbon cloth
- CFP = carbon fiber paper
- CP = carbon paper
- CM = chloro methylated
- DABCO = 1,4-diazabicyclo(2.2.2)octane

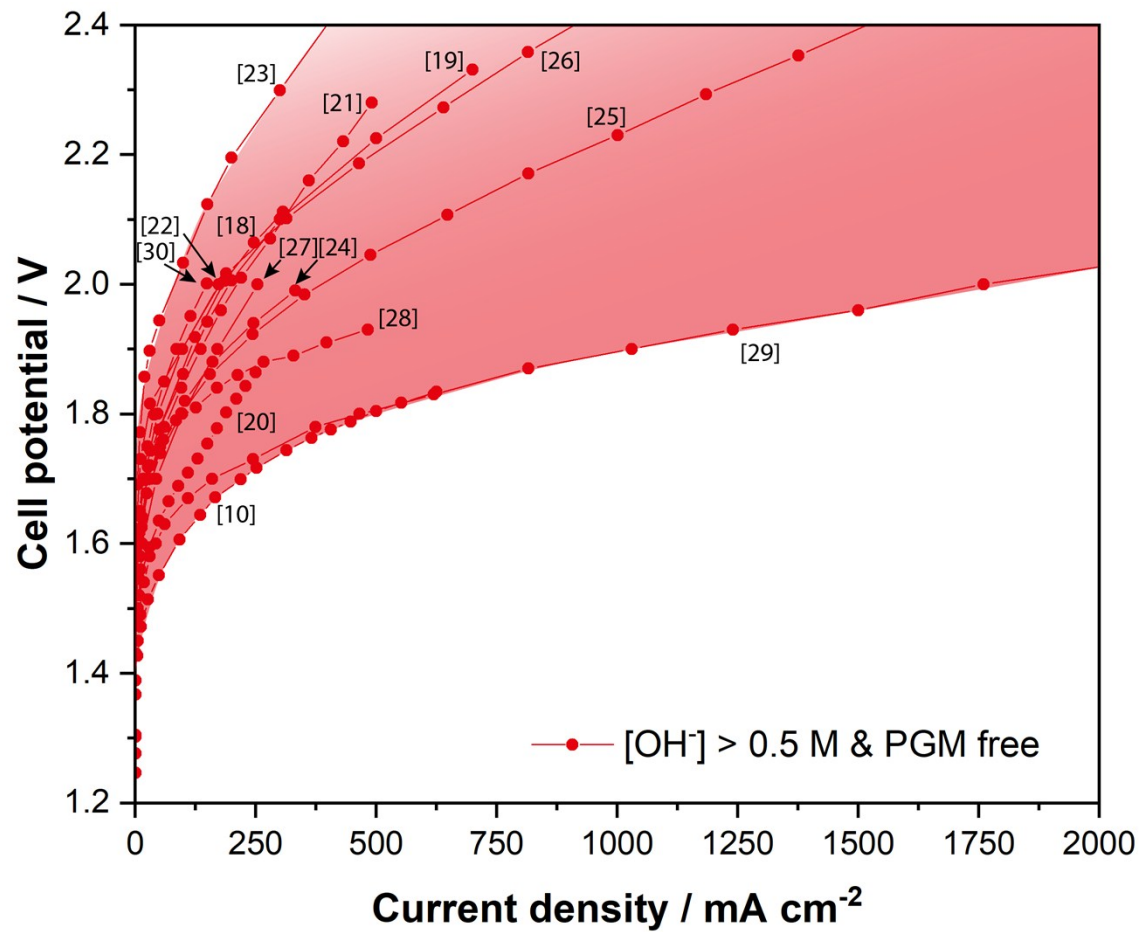
- DMAEMA = 2-dimethylaminoethyl methacrylate
- DTB = DMAEMA-TFEMA-BMA
- g = grafted
- GDE = gas diffusion electrode
- GDL = gas diffusion layer
- LDPE = low density polyethylene
- *m*-PBI = poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole)
- *mes*-PBI = poly(2,2'-(*m*-mesitylene)-5,5'-bibenzimidazole)
- mm = methylated melamine
- MPL = micro porous layer
- NF = nickel foam
- PBI = polybenzimidazole
- PEG-PPG = poly(ethylene glycol-*ran*-propylene glycol)
- PSEBS = polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene
- PSF = poly(arylene ether sulfone)
- PTFE = poly(tetrafluoroethylene)
- PVA = poly(vinyl alcohol)
- PVP = poly(vinylpyrrolidone)
- QPDTB = quaternized poly(DMAEMA-*co*-TFEMA-*co*-BMA)
- qPPO = quaternized poly(phenylene oxide)
- SS = stainless steel.
- TFEMA = 2,2,2,-trifluoroethyl methacrylate
- TMA = trimethylamine
- VBC = vinyl benzyl chloride
- xQAPS = crosslinked quaternary ammonium polysulfone.



**Figure S1:** Performance review of cells with no (or below 0.5 M) supporting hydroxide electrolyte. PGM free cells.

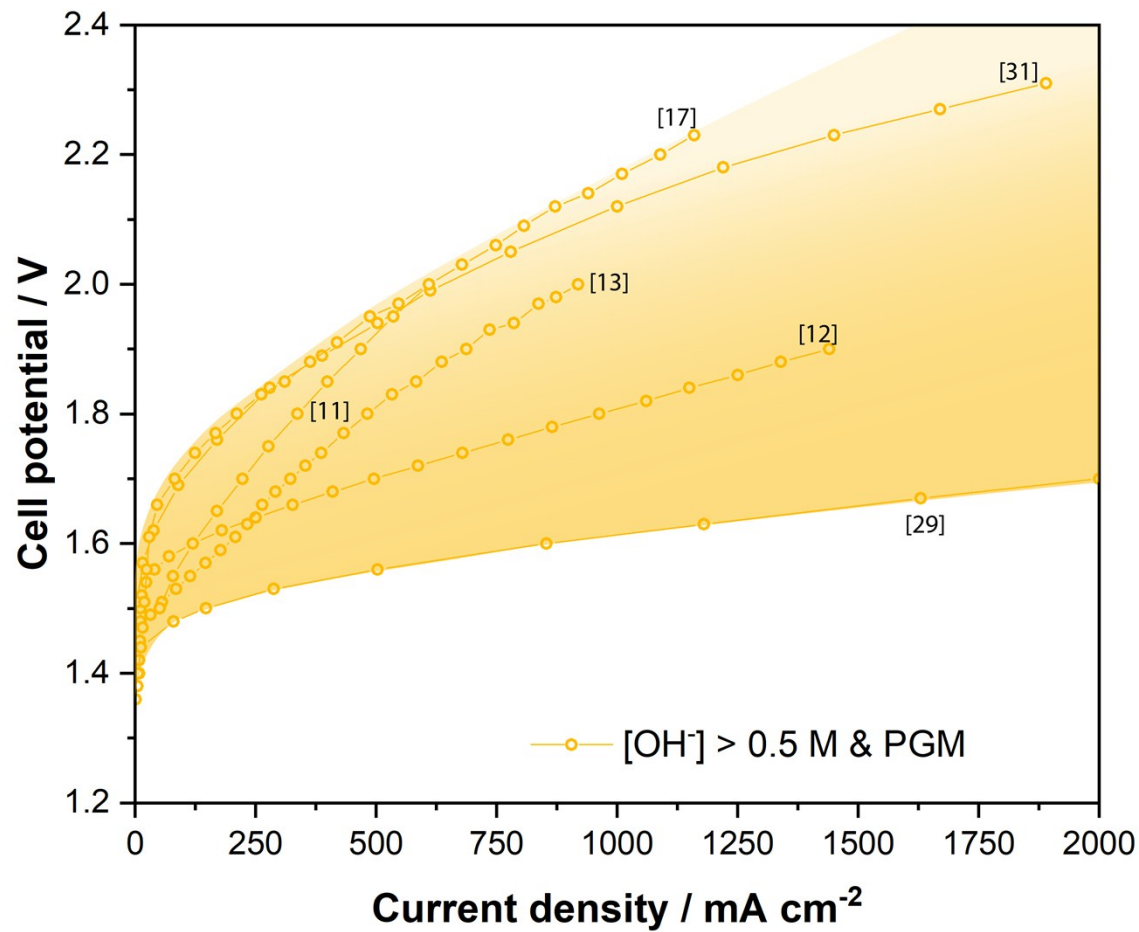


**Figure S2:** Performance review of cells with no (or below 0.5 M) supporting hydroxide electrolyte, but with PGM catalysts.

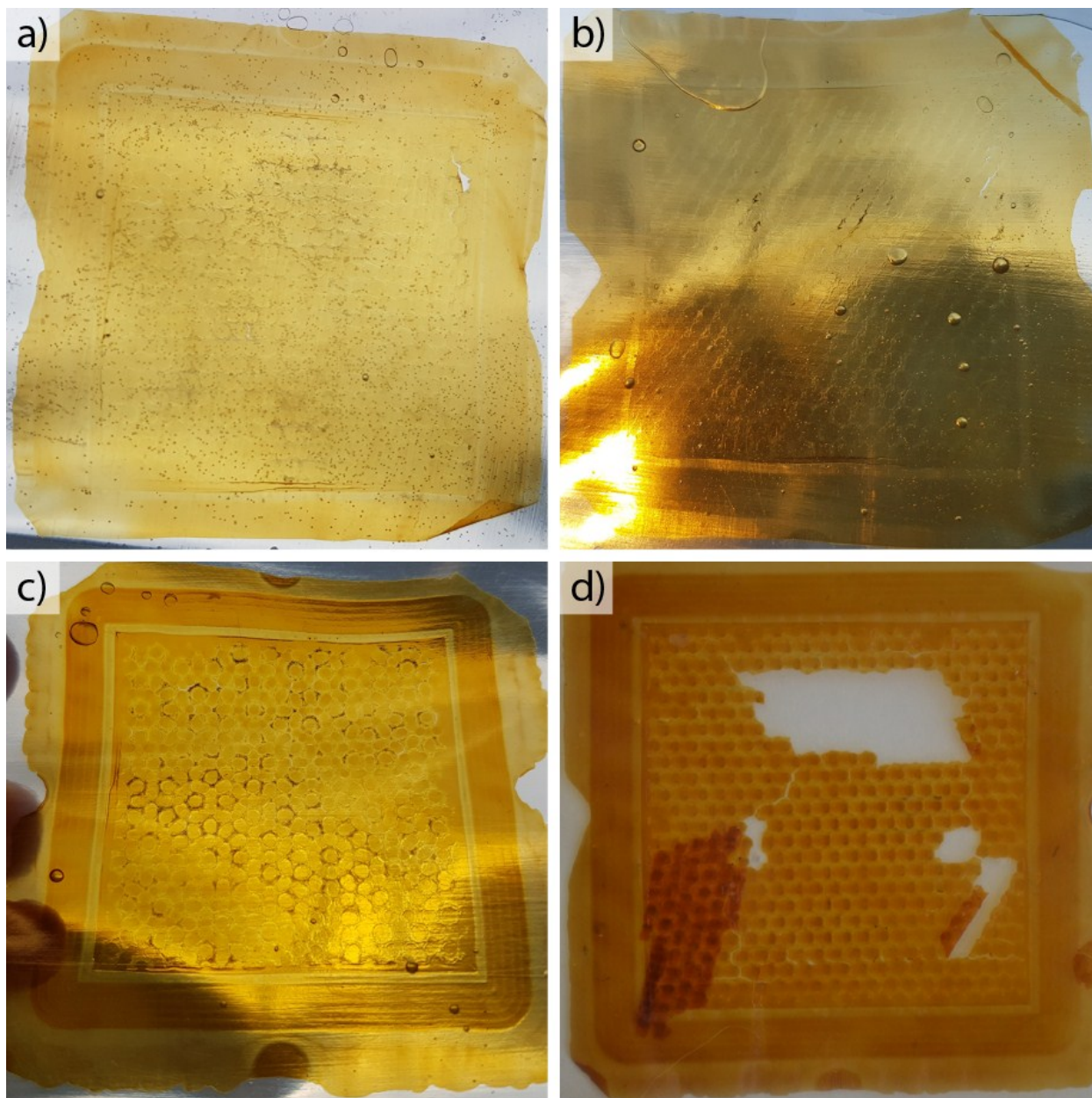


**Figure S3:** Performance review of cells with significant supporting hydroxide electrolyte. PGM free cells.

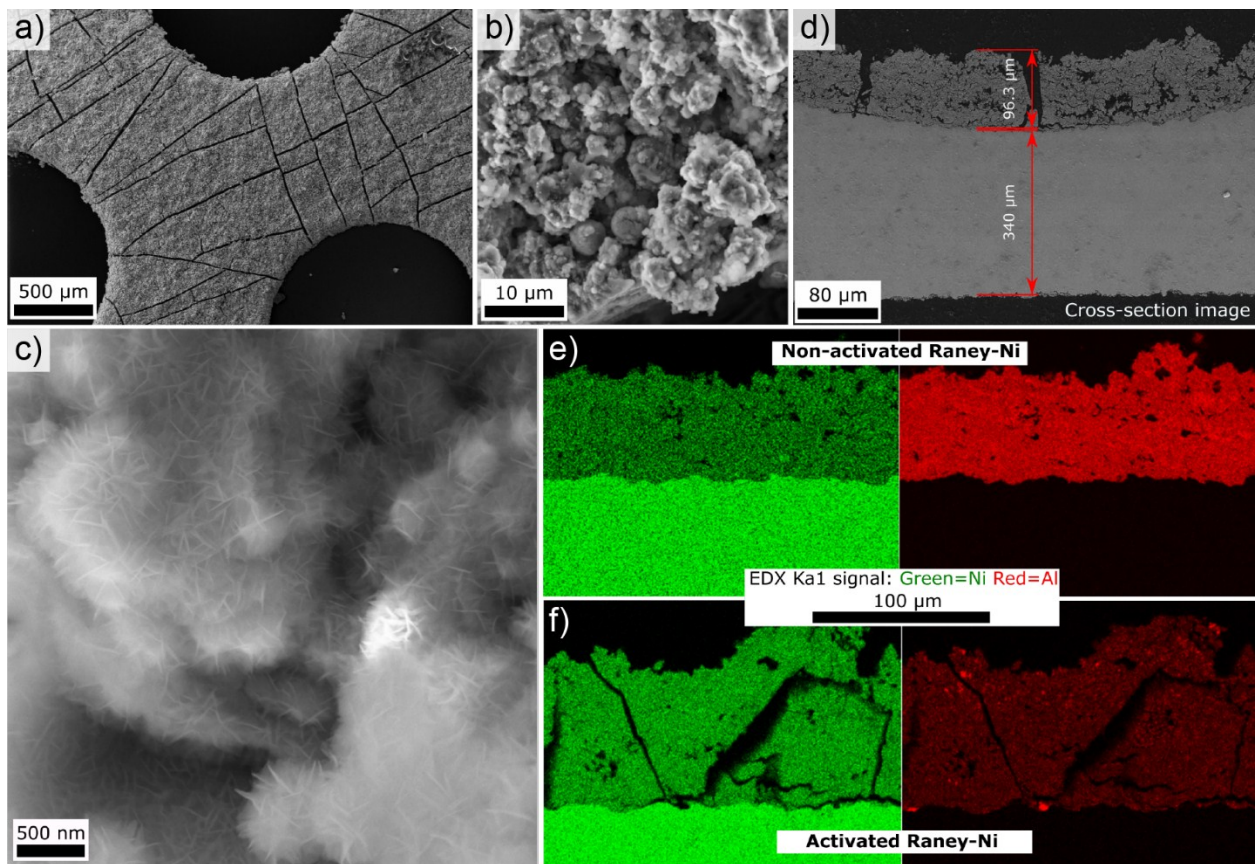




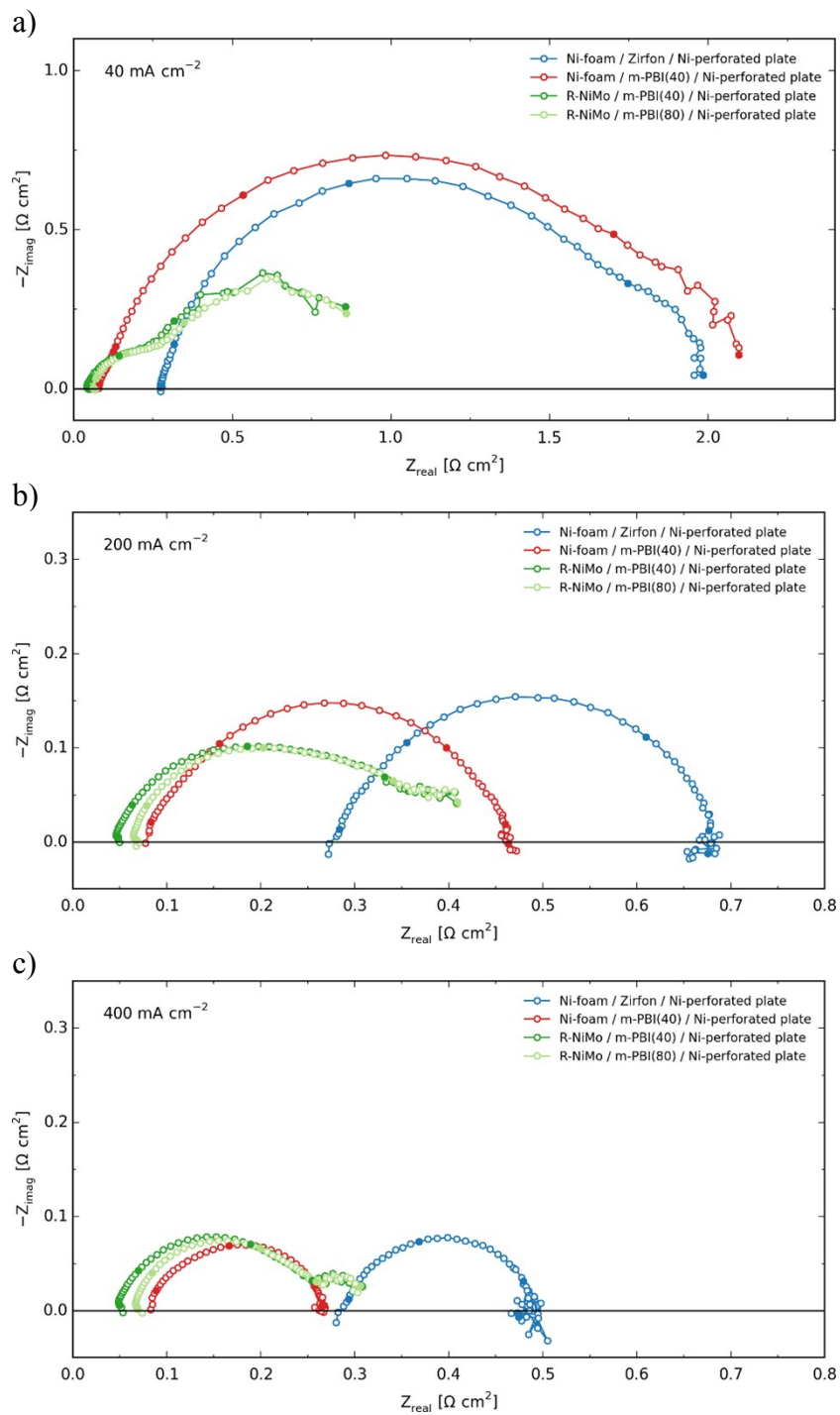
**Figure S4:** Performance review of cells with significant supporting hydroxide electrolyte and with PGM catalysts.



**Figure S5:** Photographs of damaged membranes, operated for ~148.5 h (a), ~122 h (b), ~231 h (c) and ~309 h (d). Membranes had an initial thickness of 40  $\mu\text{m}$  (a-b) and 80  $\mu\text{m}$  (c-d). The membranes were rinsed with water before being stored in sealed plastic envelopes, then photographed.



**Figure S6:** SEM of a Raney-Ni electrode (a-d) and EDX map of a Raney-Ni electrode before (e) and after activation (f).



**Figure S7:** EIS of 4 different cells (cathode / separator / anode) at  $40 \text{ mA cm}^{-2}$  (a),  $200 \text{ mA cm}^{-2}$  (b) and  $400 \text{ mA cm}^{-2}$  (c). Data points shown for frequencies between 20 kHz and 1 Hz. Decade points are marked by solid markers.  $T = 80^\circ\text{C}$ ,  $[\text{KOH}] = 24 \text{ wt}\%$ .

**Table S1:** Details of cells without supporting hydroxide electrolyte (or < 0.5 M) and without PGM catalysts.

| Reference                  | Year | Electrolyte                          | Membrane                 |                                | Ionomer/<br>binder          | Anode                  |  | Cathode                |   | Temp.              |
|----------------------------|------|--------------------------------------|--------------------------|--------------------------------|-----------------------------|------------------------|--|------------------------|---|--------------------|
|                            |      |                                      | Material                 | Thickness<br>( $\mu\text{m}$ ) |                             | PTL                    | Catalyst   | PTL                    | Catalyst  | $^{\circ}\text{C}$ |
| <b>Xiao</b> <sup>5</sup>   | 2012 | Water                                | xQAPS                    | 70                             | xQAPS                       | Ni infiltrated NF      | Electroplated Ni/Fe 1:1  | SS fiber felt          | Ni/Mo 1:2   | 70                 |
| <b>Cao</b> <sup>6</sup>    | 2012 | Water                                | mm-qPVBz/Cl <sup>-</sup> | 70                             | 20 wt% qPVB/Cl <sup>-</sup> | SS mesh & CFP          | Cu <sub>0.7</sub> Co <sub>2.3</sub> O <sub>4</sub> @ 3 mg cm <sup>-2</sup>     | SS mesh & CFP          | Ni @ 2 mg cm <sup>-2</sup>  | 55                 |
| <b>Wu</b> <sup>7</sup>     | 2012 | Water                                | "Cranfield membrane"     | n/a                            | QPDTB                       | SS mesh                | Cu <sub>0.7</sub> Co <sub>2.3</sub> O <sub>4</sub> @ 3 mg cm <sup>-2</sup>     | SS mesh                | Ni @ 2 mg cm <sup>-2</sup>  | 22                 |
| <b>Faraj</b> <sup>8</sup>  | 2012 | 1 wt% K <sub>2</sub> CO <sub>3</sub> | LDPE-g-VBC-DABCO         | 50-100                         | Tokuyama AS-4 (?)           | Sigracet CP (25BC) (?) | ACTA SpA catalyst  | Sigracet CP (25BC) (?) | ACTA SpA catalyst   | 45                 |
| <b>Wu</b> <sup>9</sup>     | 2013 | Water                                | "Cranfield membrane"     | n/a                            | QPDTB-OH <sup>-</sup>       | SS mesh                | Li <sub>0.21</sub> Co <sub>2.79</sub> O <sub>4</sub> @ 2.5 mg cm <sup>-2</sup> | SS mesh                | Ni @ 2 mg cm <sup>-2</sup>  | 45                 |
| <b>Pavel</b> <sup>10</sup> | 2014 | 1 wt% K <sub>2</sub> CO <sub>3</sub> | Tokuyama A201            | 28                             | 10 wt% PTFE                 | NF                     | CuCoO <sub>x</sub> (ACTA 3030) @ 36 mg cm <sup>-2</sup>                        | Cetech CC+MPL          | CeO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub> /C (ACTA 4030) @ 7.4 mg cm <sup>-2</sup> | 35 & 55            |
| <b>Hnat</b> <sup>11</sup>  | 2017 | 1 wt% KOH                            | PSEBS-DABCO              | n/a                            | 10 wt% PSEBS-DABCO          | NF                     | NiCo <sub>2</sub> O <sub>4</sub> @ 10 mg cm <sup>-2</sup>                      | NF                     | NiFeO <sub>4</sub> @ 10 mg cm <sup>-2</sup>   | 40                 |

**Table S2:** Details of cells without supporting hydroxide electrolyte (or < 0.5 M), but with PGM catalysts.

| Reference                     | Year | Electrolyte                       | Membrane              |                                | Ionomer/<br>binder   | Anode                          |   | Cathode               |   | Temp.<br>°C |
|-------------------------------|------|-----------------------------------|-----------------------|--------------------------------|--|--------------------------------|---|-----------------------|---|-------------|
|                               |      |                                   | Material              | Thickness<br>( $\mu\text{m}$ ) |  | PTL                            | Catalyst  | PTL                   | Catalyst  |             |
| <b>Wu</b> <sup>12</sup>       | 2011 | Water                             | n/a                   | 50                             | none   | SS mesh                        | $\text{Cu}_{0.7}\text{Co}_{2.3}\text{O}_4$ @<br>3 mg cm <sup>-2</sup>             | SS mesh               | 20 wt% Pt/C @<br>1 mg cm <sup>-2</sup> Pt           | 25          |
| <b>Leng</b> <sup>13</sup>     | 2012 | Water                             | Tokuyama<br>A201      | 28                             | 16 wt%<br>Tokuyama AS-4                                      | Ti foam                        | $\text{IrO}_2$ @ 2.9 mg<br>cm <sup>-2</sup>                                       | Toray CP<br>(H-120)   | Pt black @ 3.2<br>mg cm <sup>-2</sup>               | 50          |
| <b>Wu</b> <sup>14</sup>       | 2012 | Water                             | LDPE-g-VBC            | 160                            | n/a  | Toray CP<br>(H-090)            | $\text{Cu}_{0.6}\text{Mn}_{0.3}\text{Co}_{2.1}\text{O}_4$ @ 3 mg cm <sup>-2</sup> | Toray CP<br>(H-090)   | 50 wt% Pt/C @<br>1 mg cm <sup>-2</sup> Pt           | 40          |
| <b>Parrondo</b> <sup>15</sup> | 2014 | Water                             | PSF-TMA               | n/a                            | 30 wt% PSF-<br>TMA   | "Porous<br>media<br>electrode" | $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ @<br>2.5 mg cm <sup>-2</sup>               | Sigracet CP<br>(10BC) | Pt black @ 2.5<br>mg cm <sup>-2</sup>               | 50          |
| <b>Hnat</b> <sup>11</sup>     | 2014 | 0.5 M<br>$\text{Na}_2\text{CO}_3$ | LDPE-PEG-<br>PPG-ANEX | 300                            | 10 wt% (anode)<br>& 15 wt%<br>(cathode) qPPO                 | NF                             | $\text{NiCo}_2\text{O}_4$ @ 2.5<br>mg cm <sup>-2</sup>                            | NF                    | Pt/C @ 0.3 mg<br>cm <sup>-2</sup> Pt                | 70          |
| <b>Park</b> <sup>16</sup>     | 2018 | Water                             | Tokuyama<br>A201      | n/a                            | Tokuyama AS-4  | GDE                            | Platinum group<br>metals @ 2 mg<br>cm <sup>-2</sup>                               | GDE                   | Platinum group<br>metals @ 2 mg<br>cm <sup>-2</sup> | 50          |
| <b>Gupta</b> <sup>17</sup>    | 2018 | 0.1 M NaOH                        | LDPE-g-VBC-<br>TMA    | n/a                            | 10 wt% (anode)<br>or 28 wt%<br>(cathode)<br>PSEBS-CM-<br>TMA | Ti fibre felt                  | $\text{NiCo}_2\text{O}_4$ @ 10<br>mg cm <sup>-2</sup>                             | Carbon<br>GDL+MPL     | 20 wt% Pt/C @<br>0.4 mg cm <sup>-2</sup> Pt         | 60          |

**Table S3:** Details of cells with supporting hydroxide electrolyte (> 0.5 M), but without PGM catalysts.

| Reference              | Year | Electrolyte | Membrane               |                                | Ionomer/<br>binder    | Anode            |   | Cathode          |   | Temp.<br>°C |
|------------------------|------|-------------|------------------------|--------------------------------|-----------------------|------------------|---|------------------|---|-------------|
|                        |      |             | Material               | Thickness<br>( $\mu\text{m}$ ) |                       | PTL              | Catalyst  | PTL              | Catalyst  |             |
| Yeo <sup>18</sup>      | 1980 | 10 wt% NaOH | Nafion 115             | 120                            | -                     | Ni screen        | -   | Ni screen        | -   | 95          |
| Aili <sup>19</sup>     | 2013 | 30 wt% KOH  | Crosslinked m-PBI      | 100                            | -                     | Polished Ni      | -   | Polished Ni      | -   | 80          |
| Pavel <sup>10</sup>    | 2014 | 1 M KOH     | Tokuyama A201          | 28                             | 10 wt% PTFE           | NF               | CuCoOx (ACTA 3030) @ 36 mg cm <sup>-2</sup>               | Cetech CC+MPL    | CeO <sub>2</sub> -La <sub>2</sub> O <sub>3</sub> /C (ACTA 4030) @ 7.4 mg cm <sup>-2</sup> | 43          |
| Ahn <sup>20</sup>      | 2014 | 1 M KOH     | Tokuyama A201          | n/a                            | -                     | CP               | Electroplated Ni  | CP               | Electroplated Ni  | 70          |
| Vazac <sup>21</sup>    | 2014 | 15 wt% KOH  | Nafion 112             | 50.8                           | -                     | Ni expanded mesh | -   | Ni expanded mesh | -   | 75          |
| Schauer <sup>22</sup>  | 2015 | 10 wt% KOH  | PSU-DABCO              | 120                            | 20 wt% PTFE           | NF               | NiCo <sub>2</sub> O <sub>4</sub> @ 5 mg cm <sup>-2</sup>  | NF               | -   | 50          |
| Aili <sup>23</sup>     | 2015 | 30 wt% KOH  | Aquivion-PVP 30wt%     | 105                            | -                     | Polished Ni      | -   | Polished Ni      | -   | 80          |
| Diaz <sup>24</sup>     | 2016 | 3 M KOH     | Crosslinked AB-PBI     | 90-120                         | -                     | NF               | -   | NF               | -   | 70          |
| Kraglund <sup>25</sup> | 2016 | 25 wt% KOH  | m-PBI                  | 50-60                          | -                     | NF               | -   | NF               | -   | 80          |
| Aili <sup>26</sup>     | 2017 | 25 wt% KOH  | mes-PBI                | 60                             | -                     | NF               | -   | NF               | -   | 80          |
| Chanda <sup>27</sup>   | 2017 | 10 wt% KOH  | LDPE-PEG-PPG-ANEX      | n/a                            | 15 wt% qPPO           | NF               | NiCo <sub>2</sub> O <sub>4</sub> @ 10 mg cm <sup>-2</sup> | NF               | -   | 50          |
| Diaz <sup>28</sup>     | 2017 | 15 wt% KOH  | Crosslinked PVA-AB-PBI | 40-120                         | -                     | NF               | -   | NF               | -   | 70          |
| Liu <sup>29</sup>      | 2017 | 1 M KOH     | Sustainion X37-50      | 60                             | 10 wt% Nafion         | SS fiber felt    | NiFe <sub>2</sub> O <sub>4</sub> @ 2 mg cm <sup>-2</sup>  | Carbon GDL       | NiFeCo @ 3 mg cm <sup>-2</sup>  | 60          |
| Hnat <sup>30</sup>     | 2017 | 15 wt% KOH  | PSEBS-CM-DABCO         | n/a                            | 10 wt% PSEBS-CM-DABCO | NF               | NiCo <sub>2</sub> O <sub>4</sub> @ 10 mg cm <sup>-2</sup> | NF               | NiFe <sub>2</sub> O <sub>4</sub> @ 10 mg cm <sup>-2</sup>                                 | 40          |

**Table S4:** Details of cells with supporting hydroxide electrolyte (> 0.5 M) and with PGM catalysts.

| Reference                  | Year | Electrolyte | Membrane              |                                | Ionomer/<br>binder   | Anode                     |   | Cathode                   |   | Temp.              |
|----------------------------|------|-------------|-----------------------|--------------------------------|--|---------------------------|---|---------------------------|---|--------------------|
|                            |      |             | Material              | Thickness<br>( $\mu\text{m}$ ) |  | PTL                       | Catalyst  | PTL                       | Catalyst                                    | $^{\circ}\text{C}$ |
| <b>Wu</b> <sup>12</sup>    | 2011 | 1 M KOH     | n/a                   | n/a                            | none   | SS mesh                   | $\text{Cu}_{0.7}\text{Co}_{2.3}\text{O}_4$ @<br>3 $\text{mg cm}^{-2}$ | SS mesh                   | 20 wt% Pt/C @<br>1 $\text{mg cm}^{-2}$ Pt   | 25                 |
| <b>Li</b> <sup>31</sup>    | 2011 | 4 M NaOH    | ITM Power<br>membrane | 160                            | -  | SS mesh                   | Ni/Fe 9:1 oxide   | SS mesh                   | Pt  | 60                 |
| <b>Leng</b> <sup>13</sup>  | 2012 | 1 M KOH     | Tokuyama<br>A201      | 28                             | 16 wt%<br>Tokuyama AS-4                                      | Ti foam                   | $\text{IrO}_2$ @ 2.9 $\text{mg cm}^{-2}$                              | Toray CP<br>(H-120)       | Pt black @ 3.2<br>$\text{mg cm}^{-2}$       | 50                 |
| <b>Hnat</b> <sup>11</sup>  | 2014 | 1 M KOH     | LDPE-PEG-<br>PPG-ANEX | 300                            | 10 wt% (anode)<br>& 15 wt%<br>(cathode) qPPO                 | NF                        | $\text{NiCo}_2\text{O}_4$ @ 2.5<br>$\text{mg cm}^{-2}$                | NF                        | Pt/C @ 0.3 $\text{mg cm}^{-2}$<br>Pt        | 70                 |
| <b>Liu</b> <sup>29</sup>   | 2017 | 1 M KOH     | Sustainion X37-<br>50 | 60                             | Nafion   | Sigracet<br>GDL<br>(39BC) | $\text{IrO}_2$  | Sigracet<br>GDL<br>(39BC) | Pt  | 60                 |
| <b>Gupta</b> <sup>17</sup> | 2018 | 1 M NaOH    | LDPE-g-VBC-<br>TMA    | n/a                            | 10 wt% (anode)<br>or 28 wt%<br>(cathode)<br>PSEBS-CM-<br>TMA | Ti fibre felt             | $\text{NiCo}_2\text{O}_4$ @ 10<br>$\text{mg cm}^{-2}$                 | Carbon<br>GDL+MPL         | 20 wt% Pt/C @<br>0.4 $\text{mg cm}^{-2}$ Pt | 20                 |



**Table S5:** BET information on electrodes, before activation, after activation, and after 12 h at 40 mA cm<sup>-2</sup> and a full polarization curve measurement. Measurements were obtained on electrode pieces, and thus include bulk nickel substrate and not only the coating. <sup>a</sup> Langmuir adsorption model. <sup>b</sup> BET adsorption model.

|                              | Cathode (Raney-NiMo) / m <sup>2</sup> g <sup>-1</sup> | Anode (Raney-Ni) / m <sup>2</sup> g <sup>-1</sup> |
|------------------------------|---|---|
| Pristine <sup>a</sup>        | 0.195   | 0.142   |
| Activated <sup>b</sup>       | 37.6  | 40.0  |
| After cell test <sup>b</sup> | 33.2  | 3.59  |

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