Electronic Supplementary information

Membrane less amphoteric decoupled water electrolysis using WO₃ and Ni(OH)₂ auxiliary electrodes

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1. WO₃ characterisation



Fig. S1. SEM image for synthesized WO₃ nanopwder.



Fig. S2. XRD for synthesized WO₃ nanopowder.

2. Electrochemical properties of red-ox mediator electrodes

Before using the redox mediator in decoupled amphoteric electrolysis, cyclic voltammetry (CV) curves at different scanning rates were measured for the WO₃ electrode in 0.5M H₂SO₄ aqueous solution and NiOOH electrode in 1M NaOH solution, respectively. CV measurements were performed in a standard three-electrode cell, where the WO₃ or Ni(OH)₂ electrode was applied as the working electrode, Ag/AgCl as the reference electrode and Pt rod as the auxiliary electrode. Figure S3 (a) presents a typical CV curve for NiOOH/Ni(OH)₂ electrode in 1M NaOH aqueous solution at different scan rates. The anodic wave represents oxidation of Ni(OH)₂ electrode to NiOOH. At 5 mV/s scan rate, the wave maximum is located at 0.4 V. Increasing the scan rate causes the maximum shift to more anodic potentials reaching 0.46 V at 50 mV/s scan rate. Similar behaviour is observed with the reduction wave at cathodic currents. The minimum reduction wave at 5 mV/s scan rate is at 0.26 V and it shifts to 0.22 V at 50 mV/s scan rate.



Fig. S3. Electrochemical characterisation of Ni(OH)₂ electrode. a) CV curves at different scan rate; b) charge storage mechanism determination from peak current vs scan rate; c) Niquist plot and equivalent circuit at Ni(OH)₂/electrolyte interface.

The shift of maximum values allows determining the charge storage mechanism of $NiOOH/Ni(OH)_2$ electrodes. Charge storage can occur due to (i) surface capacitive effects governed by the capacity of the electric double layer; (ii) diffusion-limited charge transfer on electrode/electrolyte surface [1]. The last mechanism is related to battery behaviour. The lines in Figure S3 (b) are obtained by plotting the square root of the scan rate vs the maximum current of the oxidation or reduction wave. The linear trend indicates that the NiOOH/Ni(OH)₂ electrode

behaves as a battery electrode, where the diffusion-limited charge transfer mechanism is dominating.

According to the theory, specific capacity (Q in mAh) can be determined from CV curves using the following equation [2]:

$$Q(mAh) = \frac{\int i(E)dE}{2 \cdot 3.6 \cdot m \cdot v} \tag{1}$$

where v is scan rate (V/s) and m (g) is the active substances mass. At 5 mV/s scan rate, the specific capacituy of Ni(OH)₂ electrode is 78 mAh/g.

The Nyquist plot is demonstrated in Figure S3 (c). The imaginary part of the impedance is plotted versus its real component in the frequency range from 100 mHz to 10 kHz with a sinusoidal excitation signal of 10 mV. Modified Randle circuit [3] was used to fit the experimentally obtained Nyquist plot, and fitting results (red line) are in good agreement with the experiment (blue dots). The equivalent circuit is shown as an inset in the figure. In the circuit, R_s indicates the series resistance related to the resistance of the leads as well as the mutual resistance of the individual grains at the electrode matrix. R_{ct} is the charge transfer resistance between the electrolyte and the electrode. C_{dl} is double layer capacity and CPs is pseudocapacity. W is the Warburg element associated with the diffusion process. The obtained element values are summarized in Table S1.

Table S1. The fitted equivalent circuit parameters, obtained from Niquist plot in Figure S3

Parameter	Rs, Ω	Rct, Ω	Cdl, mF	Cps, mF
Value	2.34	0.22	2.5	485.7
Error, %	0.28	3.29	6.53	1.29

A similar analysis was performed for the WO₃ electrode. CV curves at different scan rates of WO₃ electrode in $0.5 \text{ M H}_2\text{SO}_4$ aqueous solutions are shown in Figure S4.



Figure S4. Electrochemical characterisation of WO₃ electrode. a) CV curves at different scan rates; b) charge storage mechanism determination from peak current vs scan rate; c) Nyquist plot and equivalent circuit at Ni(OH)₂/electrolyte interface.

In the region of anodic potential for the WO₃ electrode, a maximum is observed in each of the curves, which shifts to the anodic side from 40 mV to 144 mV by increasing the scanning speed from 5 mV/s to 50 mV/s, respectively. Maximum indicates the deintercalation of hydrogen according to the reaction $H_xWO_3 \rightarrow WO_3 + xH^+ + xe^-$.

In the region of cathodic potential there is a plateau, but no separate peak. This plateau can be attributed to the intercalation of hydrogen according to the reaction $WO_3 + xH^+ + xe^- \rightarrow H_xWO_3$. In addition to this reaction, at higher cathodic potentials, the HER reaction starts in an acidic environment. Due to the proximity of both reactions, the maximum is not well separated in the curve. One reaction passes to the other through the plateau. The dependence of the oxidation current peak versus the square root of the scan rate does not show complete linearity, indicating the characteristics of the pseudocapacitor (Figure S4 (b)).

The specific capacity for WO₃ electrode in mAh/g was obtained similarly as $Ni(OH)_2$ electrode, and at 5 mV/s scan rate, it was 96 mAh/g.

The Nyquist plot shows similar behaviour to the $Ni(OH)_2$ electrode and the equivalent scheme is similar. The parameters of the equivalent scheme are summarized in Table S2.

Table S2. The fitted equivalent circuit parameters, obtained from Niquist plot in Figure S4.

Parameter	Rs, Ω	Rct, Ω	Cdl, mF	Cps, mF
Value	1.37	0.61	0.12	162.3

Error, %	0.24	3.20	4.49	5.53

3. Qualitative analysis of produced gasses

To analyse gas purity in acid cell and alkaline cell during favourable and unfavourable cycle, a special two-chamber cell was constructed (shown in Figure S5). As shown in Figure S5, an auxiliary electrode and working electrode, gas outlet and inlet pipe are placed in each cell. The working electrodes in both cells were Pt rod electrodes, the auxiliary electrode in the acid cell was WO_3/H_xWO_3 electrode, and in the alkaline cell was a NiOOH/Ni(OH)₂ electrode. Before electrode insertion, the WO₃ electrode was recharged as a H_xWO_3 electrode and the Ni(OH)₂ electrode as NiOOH. The cells were filled with the appropriate electrolyte (acid cell - 0.5 M aqueous H₂SO₄ solution and alkaline cell – 1 M KOH aqueous solution). The gas was analysed for a single cell in both the favourable and unfavourable cycles. The second cell was operated at that time to meet the full amphoteric cell circuit.



Figure S5. Electrolysis cell used for experiments.

The gas inlet tube was immersed in the electrolyte and connected with an argon balloon equipped with a high-precision pressure reducer valve. The outlet tube connects the mass spectrometer to the cell at the level above the electrolyte. The external power supply was connected to Pt primary electrodes. Auxiliary electrodes were connected in the circuit. Before gas measurements, the cell under investigation was purged with Ar gas for 15 min. After 15 min, the argon flow was stopped, and an overpressure of 200 mbar was set. A sample of the reference gas was taken in a mass

spectrometer (approximately 3.5 ml). The third reference sample was taken as a reference throughout the experiment.

The positive terminal of the power supply was connected to the working electrode of the alkaline cell and the negative electrode to the working electrode of the acid cell. 10 mA current and 1 V threshold potential was applied to the cell and three parallel gas samples were taken and analysed. After each sample, the mass spectrometer was vacuumed so that the composition of the previous sample did not interfere with the analysis of the next sample. After a favourable cycle of gas analysis, the cell was purged with argon for 15 minutes.

The experiment of the same sequence was repeated in the unfavourable cycle with the only difference in applied threshold potential of 3.5 V. The positive terminal was connected to the acid cell working electrode and the negative electrode to the alkaline cell working electrode. Alkaline cell gas analysis was performed under the same experimental conditions.

For 100 mA measurement the only difference was in threshold potentials. In favourable cycle it was 2 V and in unfauvorable cycle -3.2 V.

Figure S6 and S7 reflects the main lines that appear in the mass spectra of produced gas in acidic cell for 10 and 100 mA current density respectively. The characteristic line of hydrogen in the mass spectra is located at 1 and 2 m/z units. For oxygen at 32 m/z has the strongest line and at 16 m/z - weaker. During the favourable cycle for 10 mA current measurement (Figure S6 a), the only significant change occurs with the hydrogen line, the pressure of which increases from $1.2 \cdot 10^{-12}$ to $2 \cdot 10^{-11}$ bar. This indicates an almost by order of magnitude increase in the volume of H₂ gas during the favourable cycle. The oxygen line remains at the level of the reference sample, indicating the absence of oxygen.



Figure S6. Mass spectrum of acid cell gas from (a) favourable cycle and (b) unfavourable cycle at 10 mA current.

During unfavourable cycle, the oxygen concentration increased, as evidenced by the increase of the O_2 line at 32 m/z units from 10^{-13} to $6 \cdot 10^{-12}$ bar. The hydrogen line at 1 and 2 m/z remained at the level of the reference sample, indicating the absence of hydrogen in the cell (Figure S6 (b)). A similar situation was observed for the 100 mA measurement in acid cell (Figure S7 a and b). In the favourable cycle, the only change is observed for the hydrogen line, which changes from $9 \cdot 10^{-13}$ to $1.35 \cdot 10^{-11}$, while the oxygen line at 32 m/z units is not visible at all, indicating an absence of oxygen (Figure S7 a). During the unfavourable cycle, the significant change in the oxygen line from 10^{-13} to $3.5 \cdot 10^{-12}$ bar can be observed. A slight change in the hydrogen line is observed at the last measurement, which indicates a negligible presence of hydrogen. This is natural, as a higher potential is provided for 100 mA, which may result in HER reactions to the WO₃ auxiliary electrode.



Figure S7. Mass spectrum of acid cell gas from (a) favourable cycle and (b) unfavourable cycle at 100mA current.

The results of alkaline cell gas analysis are shown in Figure S8 and S9 for 10 and 100 mA current respectively.



Figure S8. Mass spectrum of alkaline cell gas from (a) favourable cycle and (b) unfavourable cycle at 10mA current.

In the alkaline cell during favourable cycle, the oxygen line at 32 m/z units increases from 10^{-13} to $5 \cdot 10^{-12}$ bar indicating oxygen volume incensement (Figure S8). The hydrogen line at 1 and 2 m/z remains at the same level indicating the absence of produced hydrogen gas. In the unfavourable cycle, oxygen lines stay at the reference level, but hydrogen line at 1 and 2 m/z units increases from $1 \cdot 10^{-12}$ to $1.7 \cdot 10^{-11}$ bar. This indicates the absence of oxygen gas and the production of hydrogen gas only.



Figure S9. Mass spectrum of alkaline cell gas from (a) favourable cycle and (b) unfavourable cycle at 100 mA current.

A similar situation was observed in 100 mA mode. In the favourable cycle, only an increase in the oxygen line from 10^{-13} to $4.5 \cdot 10^{-12}$ bar is observed (Figure S9 a), while in the unfavourable cycle, an increase in the hydrogen line from $5 \cdot 10^{-13}$ to $9 \cdot 10^{-12}$ bar is observed (Figure S9 b).

 H_2 and O_2 gas concentrations in acid and alkaline cells in both directions (favourable and unfavourable) after background substruction are summarized in Table S3 for 10 mA and Table S4 for 100 mA mode.

Cycle/cell	Concentration	1 st sample	2 nd sample	3 rd sample	Average
Favourable	C _{H2} ,%	0.5	0.3	0.4	0.4
alkaline	C ₀₂ ,%	99.5	99.7	99.6	99.6
Favourable	C _{H2} ,%	99.5	99.7	99.7	99.6
acid	C ₀₂ ,%	0.5	0.3	0.3	0.4
Unfavourable	C _{H2} ,%	99.7	99.8	99.9	99.8
alkaline	C ₀₂ ,%	0.3	0.2	0.1	0.2
Unfavourable	C _{H2} ,%	0.5	0.2	0.3	0.3
acid	$C_{02}, \%$	99.5	99.8	99.7	99.7

Table S3. H₂ and O₂ gas concentration in acid and alkaline cell in both directions for 10 mA mode.

Table S4. H_2 and O_2 gas concentration in acid and alkaline cell in both directions for 100 mA mode.

Cycle/cell	Concentration	1 st sample	2 nd sample	3 rd sample	Average
Favourable	C _{H2} ,%	0.5	1.1	0.1	0.6
alkaline	C ₀₂ ,%	99.5	98.9	99.9	99.4
Favourable	C _{H2} ,%	99.9	99.9	99.9	99.9
acid	C ₀₂ ,%	0.1	0.1	0.1	0.1
Unfavourable	C _{H2} ,%	99.1	99.7	99.6	99.5
alkaline	C ₀₂ ,%	0.9	0.3	0.4	0.5
Unfavourable	C _{H2} ,%	1.5	1.0	1.1	1.2
acid	C ₀₂ ,%	98.5	99.0	98.9	98.8

4. Quantitative analyses of produced gasses

The volume displacement method was used to measure the volume of gasses produced during the operation of the electrolyser at 10 and 100 mA current. The full experimental setting is shown in Figure S10.



Figure S10. The volumetric displacement measurement setup for quantitative gas analysis. The volume displacement during the favourable cycle is demonstrated.

Displaced volume during favourable cycle is summarized in Table S5 for 10 mA measurement.

H ₂ Gas volume, ml	Time, s	Faradaic efficiency, %
0.08	70	98
0.08	71	97
0.09	77	101
0.08	70	98
0.08	72	96
0.08	71	97
0.1	93	93
0.13	108	104
0.12	103	100
0.12	104	99
Average Faradaic efficiency, %		98
Confidence interval, %		2

Table S5. Data obtained from displaced volume determination experiment during favourable cycle at 10 mA mode.

Faraday efficiency, average from 10 independent measurements is 98±2%.

The data from unfavourable cycle are summarised in Table S6. The obtained Faradaic efficiency is the same as in favourable cycle indicating stable conversion of red-ox mediator auxiliary electrodes. The result is $98 \div 4\%$.

H ₂ Gas volume, ml	Time, s	Faradaic efficiency, %
0.07	60	100
0.09	79	98
0.08	77	90
0.08	70	98
0.09	72	108
0.08	71	97
0.09	85	91
0.1	85	101
0.08	70	98
0.07	65	93
Average Faradaic efficiency, %		98
Confidence interval, %		4

Table S6. Data obtained from displaced volume determination experiment during unfavourable cycle at 10 mA mode.

Table S7. Data obtained from displaced volume determination experiment during favourable cycle at 100mA mode.

H ₂ Gas volume, ml	Time, s	Faradaic efficiency, %
0.11	10	96
0.1	9	98
0.08	7	100
0.1	9	95
0.11	10	98
0.09	8	97
0.09	8	97
0.1	9	96
0.12	11	96
0.09	8	97
Average Faradaic efficiency, %		97
Confidence interval, %		1

Table S8. Data obtained from displaced volume determination experiment during unfavourable cycle at 100mA mode.

H ₂ Gas volume, ml	Time, s	Faradaic efficiency, %
0.10	9	95
0.08	7	98
0.14	12	103
0.12	11	93
0.13	12	91
0.11	10	97

0.10	9	97
0.10	9	91
0.09	8	9
0.08	7	100
Average Farada	96	
Confidence	2	

5. 100mA chronopotentiometry measurements



Figure S11. Chronopotenciometry measurements for 10 cycles at 100 mA current.

6. Chronopotentiometry measurements for decoupled amphoteric electrolyser operating using AEs on carbon mat substrate at different electrolysis currents



Figure S12. Favorable and unfavorable cycle using AEs on carbon mat substrate at different currents.



7. Fatigue investigation for Ni(OH)₂ and WO₃ electrode materials.





Figure S14. Chronopotentiometry measurements for WO₃ on carbon mat in single alkaline cell showing applied voltage and cycle time as a function of time and cycle number.

References

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