## **Supporting information**

## Using nickel-molybdenum cathode catalysts for efficient hydrogen gas production in microbial electrolysis cells

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**Figure S1.** NiMo Elec synthesis. (A) Photo of the cell configuration for the NiMo Elec preparation and (B) photo of the deposited NiMo on the graphite block. The NiMo Elec was collected from the bottom of the beaker and gently scraped from the graphite block before being washed, dried, and analyzed with XPS.

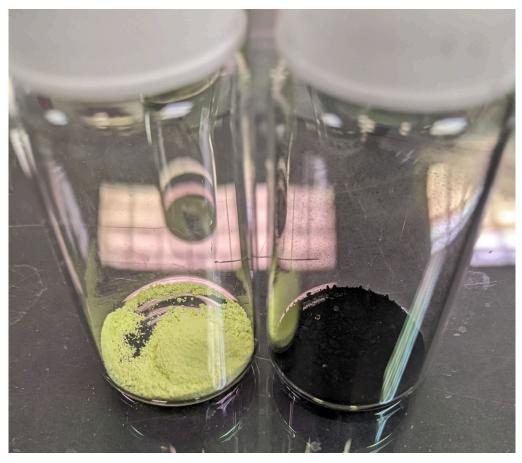


Figure S2. Photo of the NiMo Ht precursor (left) and synthesized catalyst (right) after the furnace step.

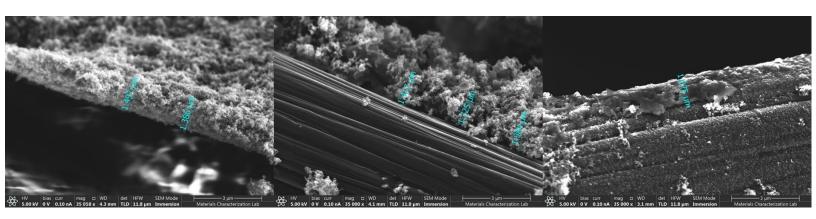
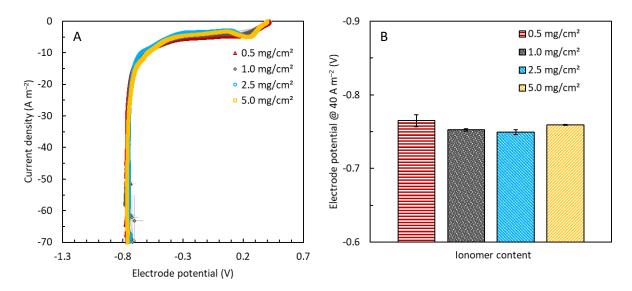
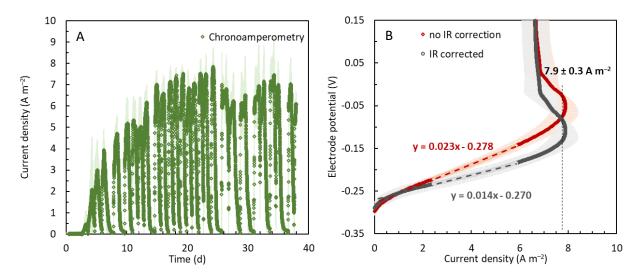


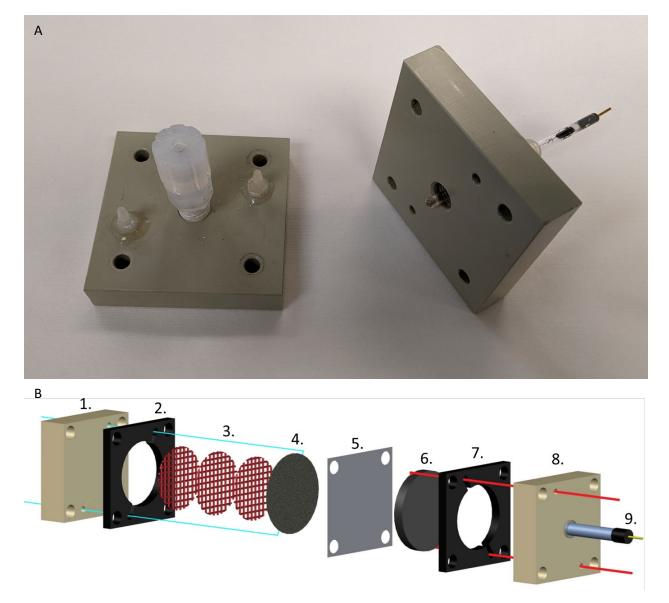
Figure S3. Examples of typical catalyst layer thickness on the different cathode samples.



**Figure S4.** Impact of the ionomer content in the cathode catalyst layer on the performance. (A) LSVs of the cathode with a variable concentration of ionomer ranging from 0.5 mg/cm<sup>2</sup> to 5.0 mg/cm<sup>2</sup> and (B) corresponding electrode potential at a current density of 40 A/m<sup>2</sup>.



**Figure S5.** Carbon felt anode performance. (A) acclimation and (B) LSV corrected and not corrected for the ohmic resistance. The cell configuration can largely influence the anode performance. In the cubic cell configuration, the bioanode had a resistance of 23 m $\Omega$  m2 and a limiting current density of 7.9 ± 0.3 A/m2. By using our flow-through MEC with a vapor anode the anode resistance was reduced to 1.4 ± 0.2 m $\Omega$  m<sup>2</sup> with a limiting current density of 48.2 ± 0.2 A/m<sup>2</sup>. The lower resistance coupled with a higher limiting current was due to the enhanced transport of hydroxide ions directly on the bioanode surface, which limited anode acidification and improved the electrochemical performance.



**Figure S6.** (A) Photo of the modified end plate to allow insertion of the reference electrode in the duplicate MECs. Each end plate was used in an MEC. After assembly, the reference electrode was slowly slide in the housing until the tip touched the carbon felt anode. (B) Schematic of the flow cell including the reference electrode inserted in the anode end-plate. 1., cathode end-plate; 2., cathode gasket; 3., cathode spacers; 4., cathode; 5., AEM; 6., carbon felt anode; 7., anode gasket; 8., anode end-plate with reference electrode insert; 9., reference electrode.

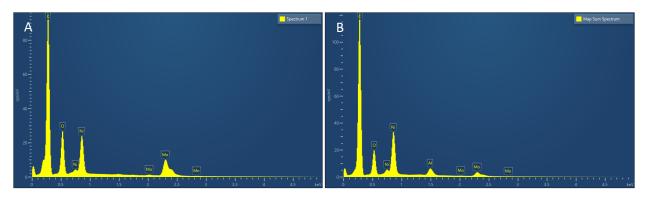
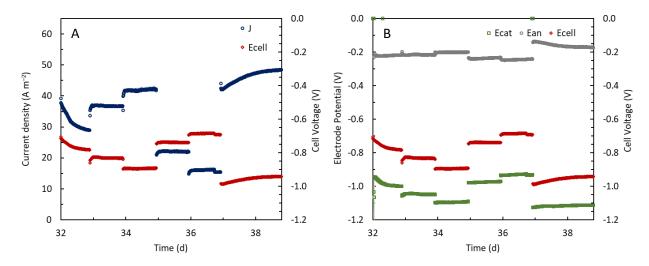
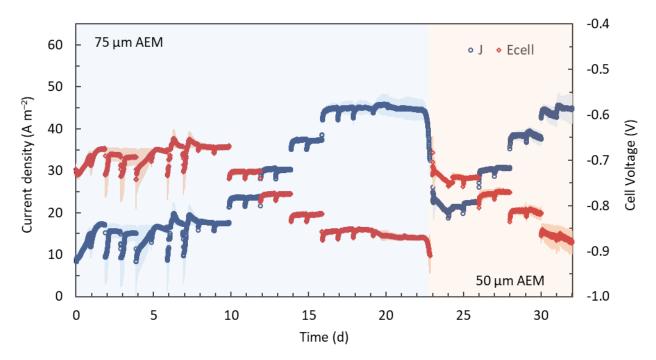


Figure S7. EDS analysis of the NiMo cathode catalysts. (A) NiMo Ht and (B) Ni Mo Elec.



**Figure S8.** MEC performance during polarization test. (A) MEC current density and cell voltage and (B) corresponding anode and cathode potentials.



**Figure S9.** MEC performance over time. The MEA was changed after 23 days of operation and the 75  $\mu$ m AEM was replaced with a new 50  $\mu$ m AEM. After 32 days from startup, the MEA was changed again back to 75  $\mu$ m AEM and the polarization curve was recorded (Figure S8)