Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels. This journal is © The Royal Society of Chemistry 2019

3D-Printed Electrodes for Membraneless Water Electrolysis

Supporting Information

Justin C. Bui, Jonathan T. Davis and Daniel V. Esposito^

Columbia University in the City of New York

Department of Chemical Engineering

Columbia Electrochemical Energy Center

Lenfest Center for Sustainable Energy

500 W. 120th St., New York, NY 10027

^corresponding author: de2300@columbia.edu

Table of Contents

S1. Volumetric Collection Efficiency Image Analysis	2	
 S2. Scanning Electron Microscopy of 3D-Printed Ni-PLA Mesh Electrode S3. Stability of Nickel Oxide Layer on 3D-Printed Electrodes S4. Tafel Analysis of 3D-Printed Ni-PLA Electrodes S5. Impedance of a 3D-Printed Ni-PLA Electrode Pair S6. HSV Analysis of Electrolyzer at Various Applied Current Densities S7. Volumetric Collection Efficiency Measurement S8. Finite Element Modeling of Current Distributions 	2 3 4 5 5	
		6

S1: Volumetric Collection Efficiency Image Analysis



Figure S1: Still-frame image from Faradaic collection experiment depicting hydrogen and oxygen collection volumes.



S2: Scanning Electron Microscopy of 3D-Printed Ni-PLA Mesh Electrode

Figure S2: SEM images of the front face of the 3D-printed nickel, asymmetric mesh electrode. (a) Low resolution SEM of front face. (b) EDS image at low resolution, demonstrating uniform deposition of nickel. (c,d) Higher resolution images of front face, depicting deposition morphology of nickel onto the carbon-PLA substrate at the micro-scale.



S3: Stability of Nickel Oxide Layer on 3D-Printed Electrodes

Figure S3: Charge density associated with the Ni oxidation redox feature in the CV curve of Figure 4 of the main text as a function of cycle number. The charge density was determined by integrating the oxidation current in the potential range associated with the nickel oxidation peak between 1.5 V vs. RHE and 1.7 V vs. RHE during the negative scan to avoid convolution with the OER signal in the forward scan.

S4: Tafel Analysis of 3D-Printed Ni-PLA Electrodes



Figure S4: Tafel analysis of (a) hydrogen evolution and (b) oxygen evolution on 3D-printed nickel electrodes. Cyclic voltammetry was run in 1.0 M NaOH on 3D-printed nickel electrodes against a nickel counter electrode and a mercury oxide reference (HgO) electrode at a scan rate of 10 mV s⁻¹. Chronoamperometry was run for 10 minutes at 0.55 V vs. HgO to passivate a nickel oxyhydroxide layer prior to the CV. Electrochemical impedance spectroscopy was used to determine a series resistance of 0.88 Ω , and the IR corrected overpotential was plotted against the log₁₀ of the current density in units of mA cm⁻². Current density was normalized based on geometric 2D-area. The Tafel slopes were then determined by performing linear regression on these plots over the range of potentials indicated by the blue lines. Curves were IR-corrected based on the EIS-measured series resistance.

S5: Impedance of 3D-Printed Electrodes



Figure S5: a.) Schematic of the 3-electrode cell used for measuring the series resistance stability of an electrode pair with the reference electrode placed in between the working and counter electrodes. **b.)** Electrochemical impedance spectroscopy (EIS) data of a single electrode pair before (colored in black) and after (colored in blue) a 4-hour stability test at an applied current density of 20 mA cm⁻². Series resistances were determined by the real-axis intercepts of linear fits to the data between 0.65 Ω and 0.9 Ω for t = 0 and between 0.7 Ω and 1.0 Ω for t = 4 hours. Due to the central placement of the reference electrode with respect to the cathode and anode, the total series resistance of the device is approximated to be two times the measured series resistance between the working and reference electrodes. The increase in series resistance for the device during this experiment is thus determined to be 0.26 Ω .



Figure S6: EIS of **a**) a single 3D-printed electrode pair measured in a two-electrode configuration and **b**) the entire six-electrode device in 1.0 M NaOH. The series resistance was determined to be $R_s = 0.98 \Omega$ and $R_s = 0.50 \Omega$, respectively, based on extrapolation of the linear portion of the curve to the x-intercept. Linear fits were performed in the ranges of $Re(Z) = 1.2 \Omega$ to 2.2 Ω and Re(Z) =0.55 Ω to 1.1 Ω for the two and six electrode configurations, respectively.





Figure S7: Still frame of the top portion of one electrode pair at the start of chronopotentiometry experiments conducted at constant current densities of **a**) 20 mA cm⁻², **b**) 50 mA cm⁻², and **c**) 75 mA cm⁻². The amount of direct crossover of bubbles between the electrode gap visibly increases with increased current density.

S7: Volumetric Collection Efficiency Measurement



Figure S8: Volume of product gas collected as a function of time. Data was recorded for an operating current density of 20 mA cm⁻². The solid lines represent the theoretical volumetric collection based on Faraday's law and the ideal gas law, while the grey dashed lines are linear fits to the experimental data.

S8: Finite Element Modeling of Current Distributions

The primary current distribution was modeled for angled electrodes using COMSOL Multiphysics software. The governing equations and boundary conditions for the simulation are described in section 2.6 of the main text. A simulation of the primary current distribution only accounts for the ohmic resistance in the electrolyte, but in reality, the current distribution will also be dependent on the solid-state electronic resistance of the electrodes, the charge transfer resistances associated with the electrochemical reactions, and mass transfer losses. In this study, the electrodes were coated with a metallic nickel layer of sufficient thickness (24 µm) such that the ohmic resistance losses of electronic conduction through this layer were negligible compared to the ohmic resistance losses in the electrolyte. This is a valid assumption because the conductivity of nickel metal is several orders of magnitude greater than the conductivity of the electrolyte. However, if a 3D printed electrode does not have this thick metal layer and has an overall resistivity that is comparable to the electrolyte, the current density will likely be nonuniform. In such a case, the local current density may be greatest near the point of contact with the charge collector or potentiostat.

The relevance of charge transfer resistance for determining current distribution can be calculated using the Wagner number (Wa).¹ This requires an understanding of the kinetics at the electrode surface. At large overpotentials the electrode half reaction can be described by Tafel kinetics and Wa can be defined as shown in Equation 1 below, where κ is the conductivity of the electrolyte, β is the Tafel slope of the electrode half reaction, *i* is the average current density of the electrode, and *l* is the characteristic length of the electrochemical cell, which in this case was chosen to be the electrode separation distance at the bottom of the cell.

$$Wa = \frac{\beta\kappa}{|i|l} \tag{1}$$

Wa describes the magnitude of the charge transfer resistance relative to the ohmic resistance. As Wa approaches zero, the charge transfer resistance becomes negligible and the primary current distribution accurately describes the system. The charge transfer resistance becomes more relevant as the magnitude of Wa approaches 1. Calculating Wa requires knowledge of the Tafel slope, and is a property of the electrode material and is specific to the half reaction and the concentration of species present. In 1.0 M NaOH, the Tafel slope on Ni for HER is 105 mV dec⁻¹ (Figure S4a) and for OER is 157 mV dec⁻¹ (Figure S4b). Given an overall electrolyte conductivity of 183.5 mS cm⁻¹,² a maximum electrode separation distance of 4.7 cm and an average current density of 20.0 mA cm⁻², Wa is calculated to be 0.20 at the cathode and 0.31 at the anode. These values indicate that the charge transfer resistance cannot be entirely ignored at low current densities, for which the actual current distribution will be more uniform than what is solved for when using the primary current distribution model. However, the primary current distribution is still useful for understanding the performance of the device in scaled up conditions where Wa will be smaller, such as at higher average current densities, longer electrode lengths, and perhaps even using more efficient electrocatalysts with larger Tafel slopes.

Over extended periods of operation, concentration gradients can also form if there is no circulation or replenishing of the electrolyte. In 1.0 M NaOH, the concentration is high enough such that no concentration gradients or diffusion boundary layers are expected to form over the duration of the experiments conducted in this report. Enhanced transport due to the free convection of bubbles detaching from the electrodes can also assist in mixing the electrolyte and ensure that no significant concentration gradients form. A more complete analysis could be conducted for

extended periods of operation to determine if circulation would be necessary to prevent efficiency losses due to a concentration overpotential. Mass transfer limitations can also affect the current distribution, with local current density expected to be inversely related to the local thickness of the diffusion boundary layer.

Figure S9 shows the results of the primary current distribution simulated in COMSOL. The potential field in the electrolyte is shown in Figure S9a. The local potential in the electrolyte is normalized relative to the total voltage drop across the electrolyte, V. Although the magnitude of the applied voltage will affect the magnitude of current density passing through the electrolyzer, it will not affect the profile of the primary current distribution. This current distribution profile is shown in Figure S9b, with the local current density normalized to the average current density passing through the electrode. The local current density is plotted as function of position along the length of the electrode, L.



Figure S9: (a) Simulated potential field of the six-electrode geometry present in the 3D-printed device. (b) Simulated primary current density distribution of a single electrode. x/L = 0 corresponds to the top of the electrode.

References:

1. Newman, J. & Thomas-Alyea, K. E. Electrochemical Systems. (John Wiley and Sons, Inc., 2004).

2. Tables. Table of Conductivity Vs Concentration for Common Solutions. 5–6 (1999).