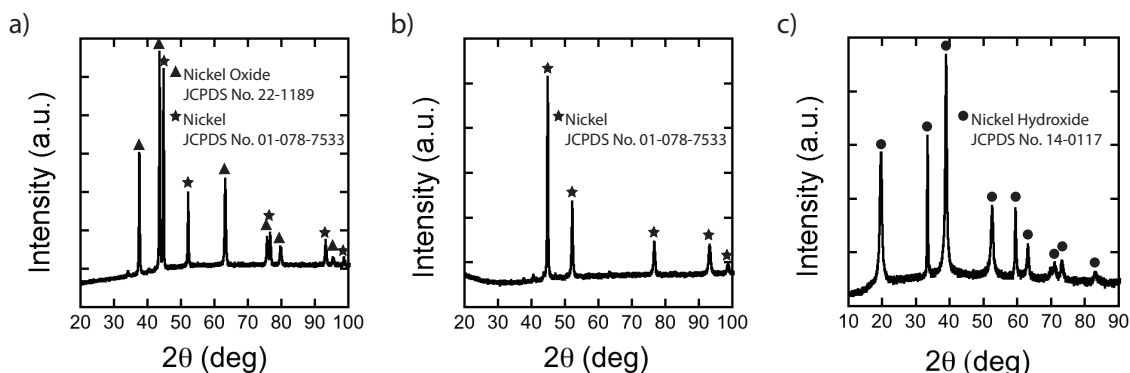


### Supplementary Information For

Microstructural tunability of co-continuous bijel derived electrodes to provide high energy and power densities

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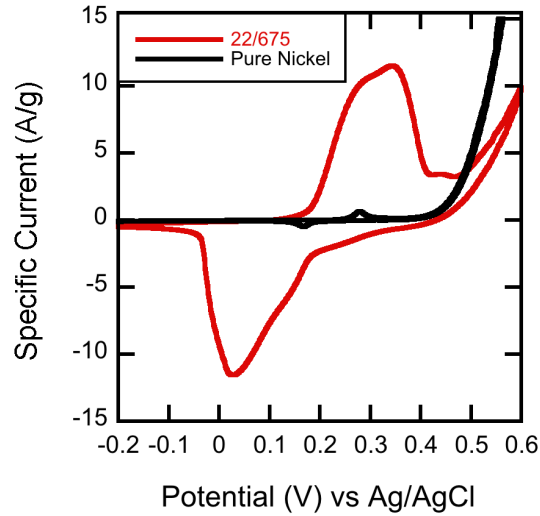


**Figure S1.** X-ray diffraction pattern of a) nickel shell sintered under air, b) nickel shell after being reduced under H<sub>2</sub>, and c) nickel hydroxide

The XRD pattern of the nickel shell after being sintered in air is shown in Fig. S1a. The pattern can be indexed to JCPDS card #22-1189 (nickel oxide) and JCPDS card # 01-078-7533 (nickel), clearly showing that some of the nickel is oxidized to NiO when sintered under air. In order to reduce the NiO to nickel, the sample was reduced under H<sub>2</sub> (4% in Ar). The XRD pattern of this step (Fig. S1b) can be indexed to JCPDS card # 01-078-7533 (nickel), showing that all the nickel oxide was reduced to nickel. Finally, the XRD pattern of free particles formed during the CBD of the nickel hydroxide formation is shown in Fig. S1c, and can be indexed to JCPDS card #14-0117 ( $\beta$ -Nickel Hydroxide).

**Table S1.** Table of the active material loading on each electrode.

Electrode	Mass Ni(OH) <sub>2</sub>
8/675	0.2 mg
8/1000	0.7 mg
15/475	0.55 mg
15/675	0.19 mg
15/1000	1.3 mg
22/675	0.11 mg
22/1000	0.3 mg



**Figure S2.** CV plot of the 22/675 Ni/Ni(OH)<sub>2</sub> composite electrode (red line) and a pure nickel shell (black line) at a scan rate of 25 mV/s.

### Calculations of specific capacitances

The specific capacitance of the electrodes can be calculated from the CV curves using the following equation:

$$\text{Specific Capacitance}(C_s) = \frac{\int_{V_1}^{V_2} i(V) dv}{\Delta V v m}$$

Where  $\Delta V$  (V) is the applied potential window,  $v$  ( $\text{Vs}^{-1}$ ) is the scan rate, and  $m$  (g) is the mass of the active material.

The specific capacitance of the electrodes can also be calculated from the galvanostatic discharge curves, using the equation below:

$$\text{Specific Capacitance}(C_s) = \frac{I \Delta t}{m \Delta V}$$

Where  $I$  (A) is the discharge current,  $\Delta t$  is the time for a full discharge,  $m$  (g) is the mass of the active material, and  $\Delta V$  (V) is the potential window.

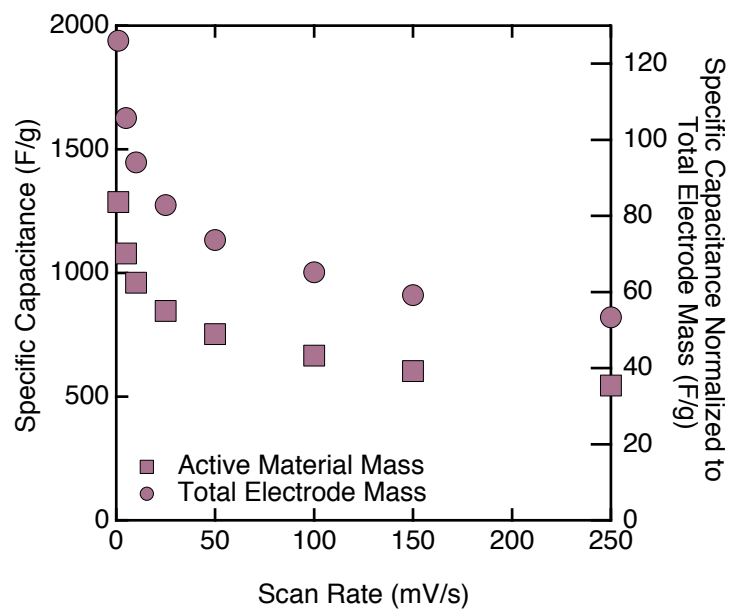
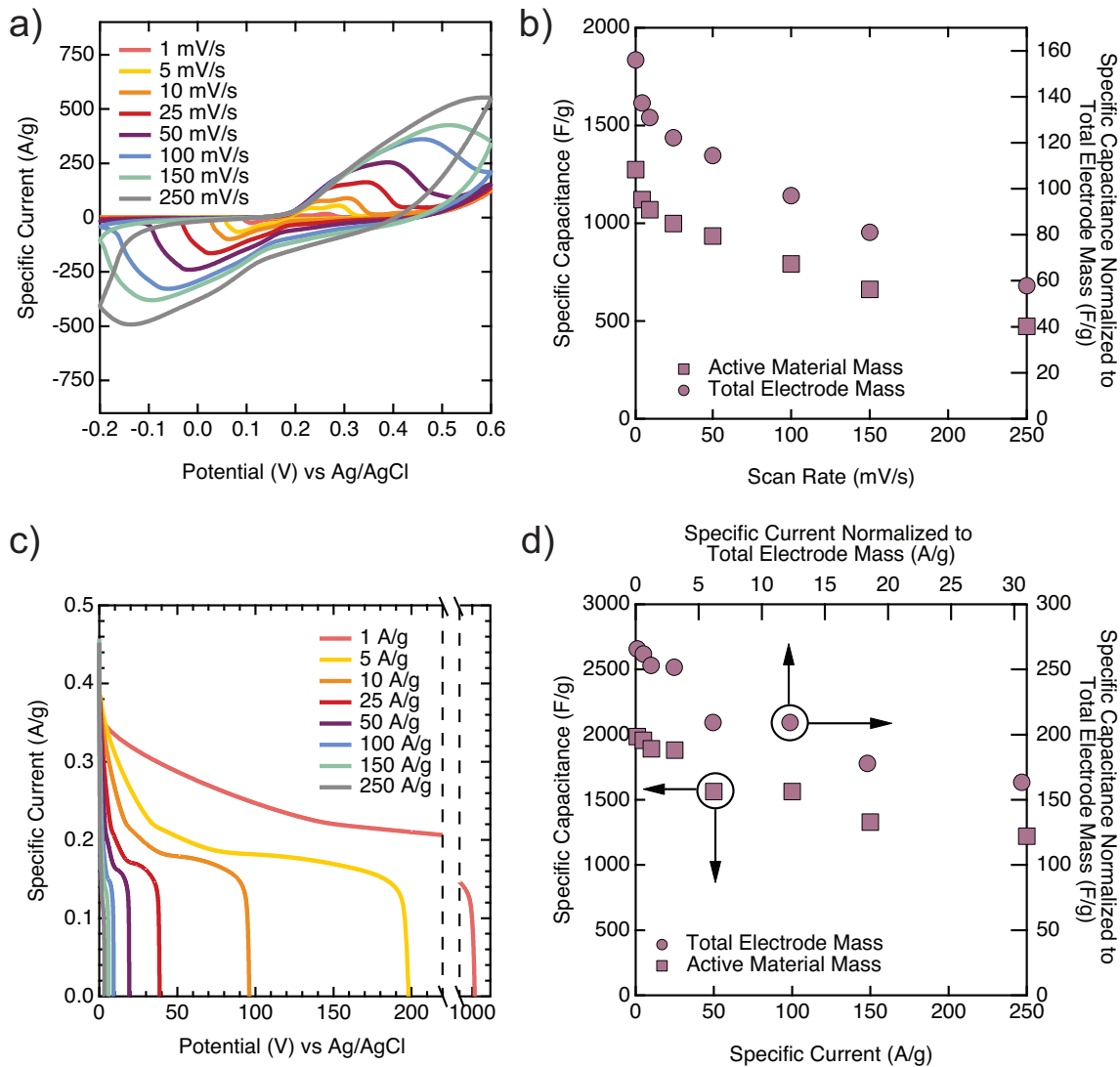
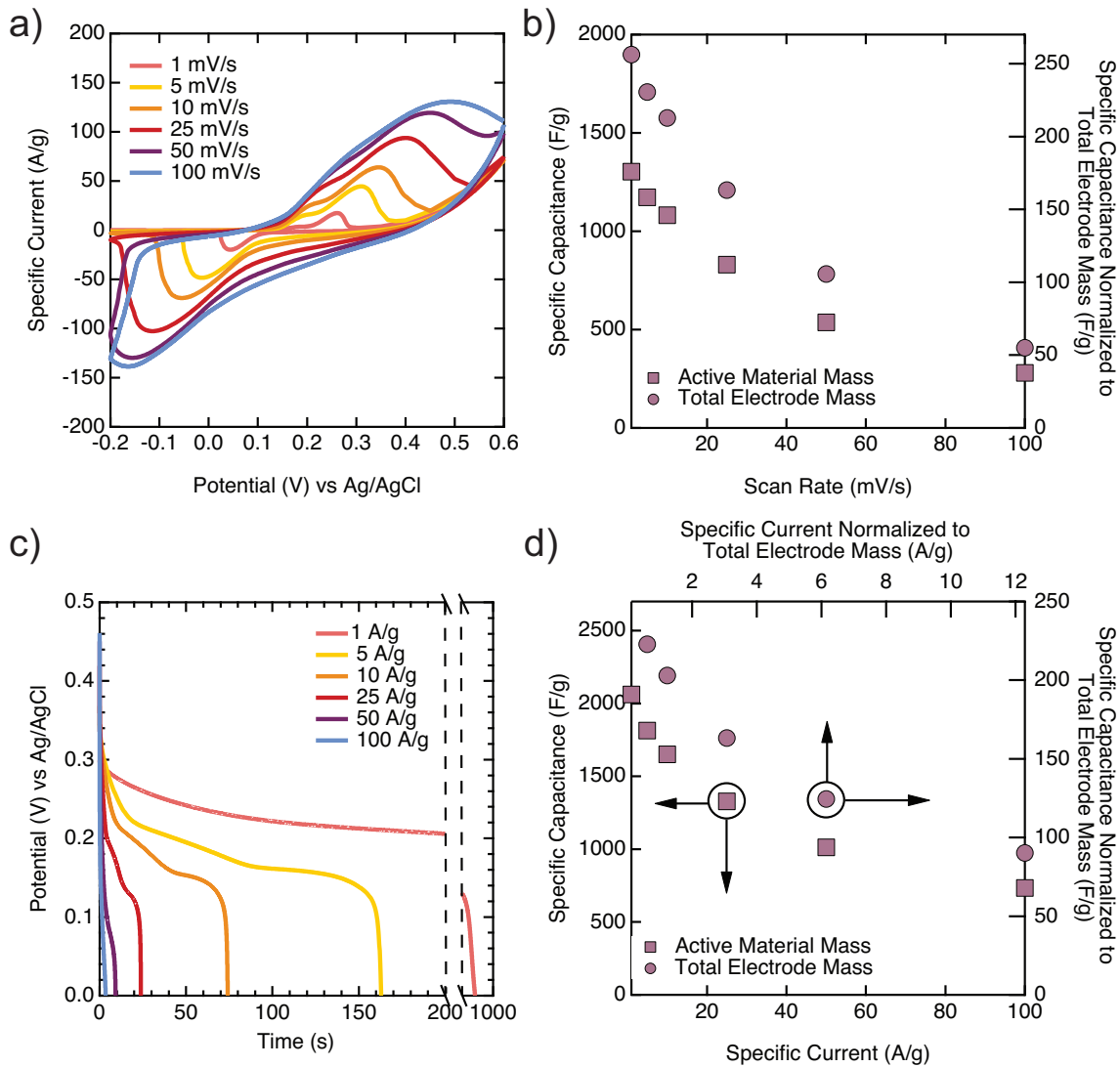


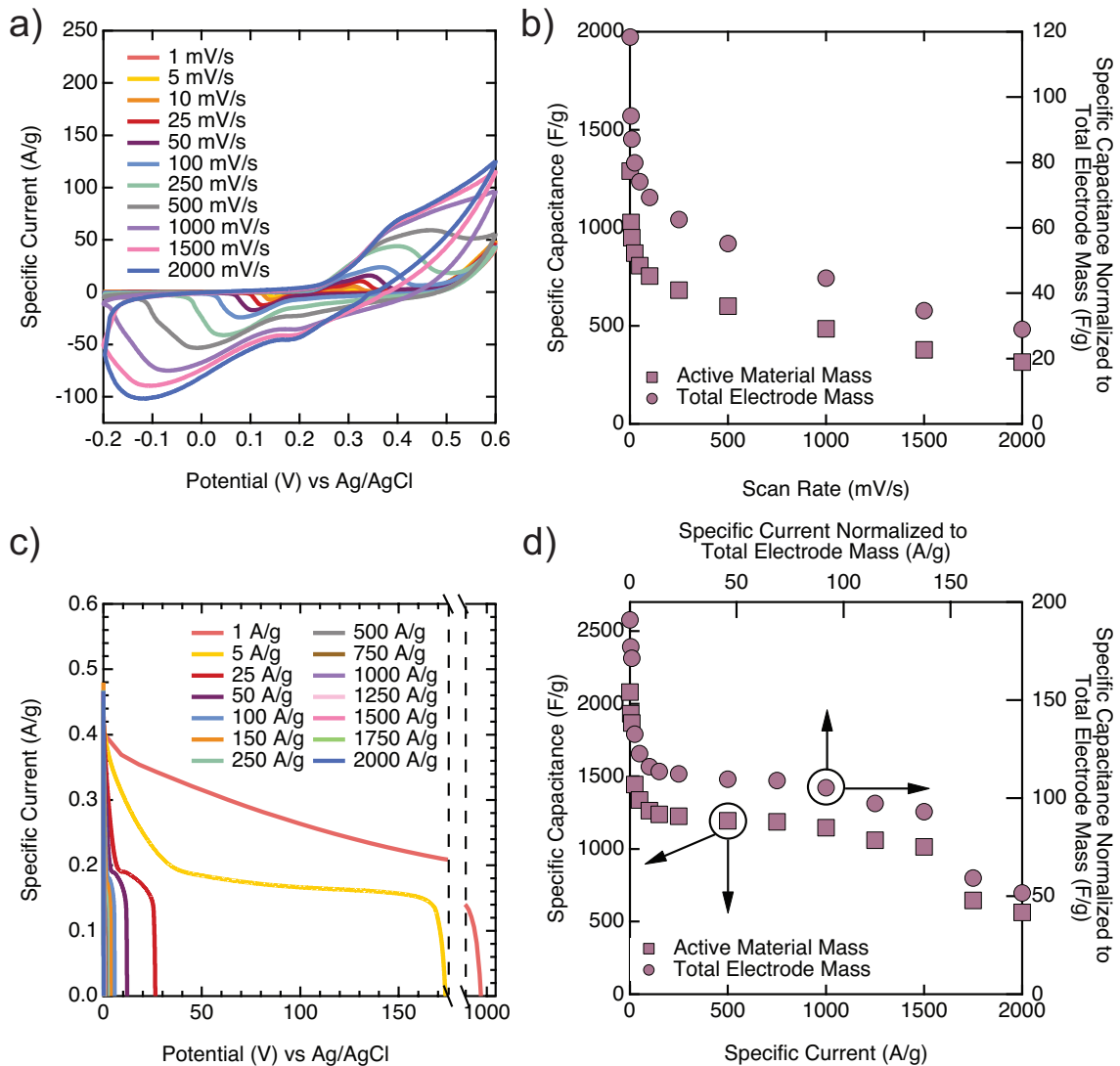
Figure S3. Gravimetric specific capacitance values of the 22/675 electrode as a function of scan rate.



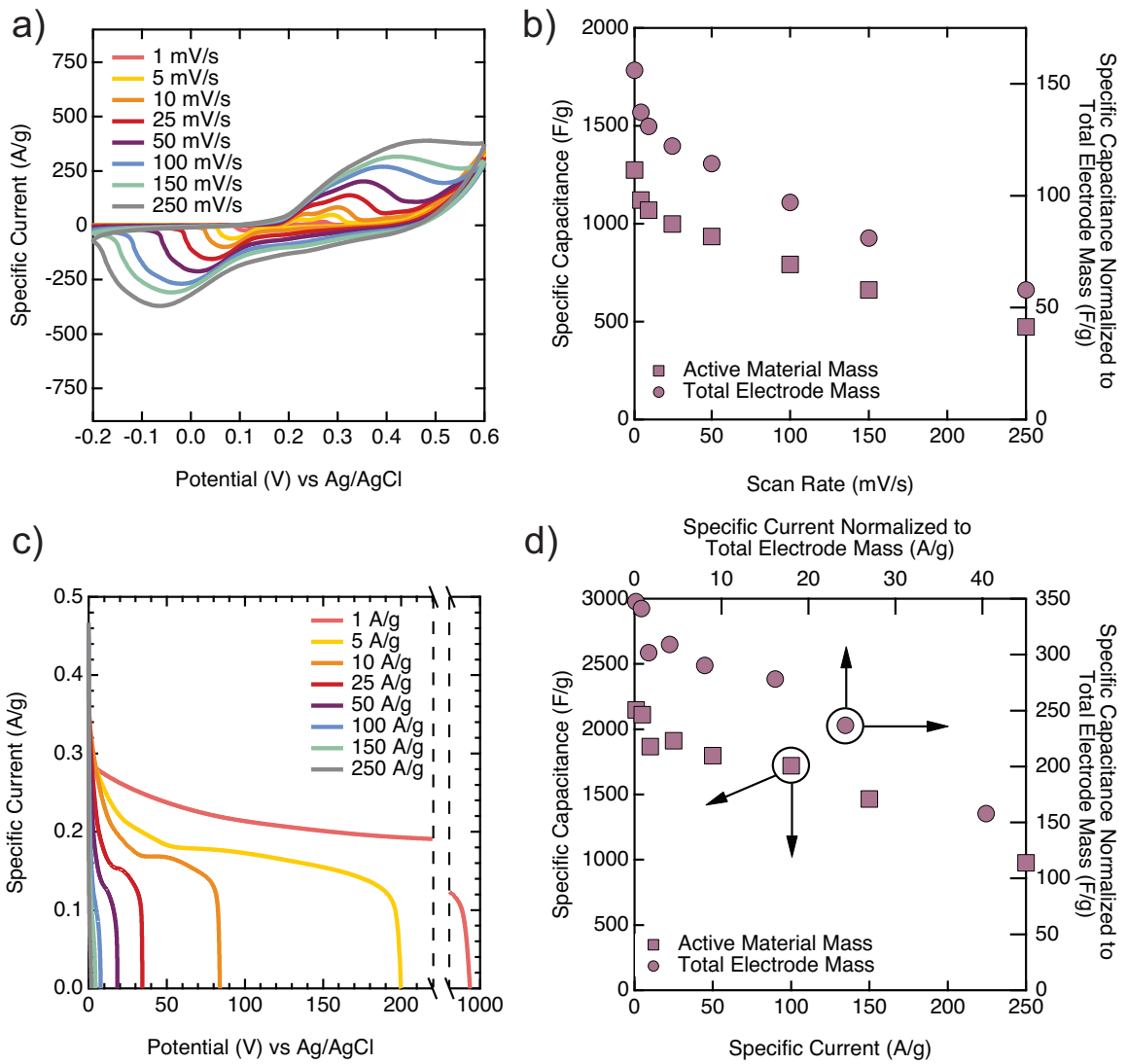
**Figure S4. Electrochemical measurements of the 8/675 Ni/Ni(OH)<sub>2</sub> composite electrode. (a) CV curves at various scan rates; (b) gravimetric specific capacitance values as a function of scan rate; (c) galvanostatic discharge curves at various current densities; (d) gravimetric specific capacitance values as a function of current density.**



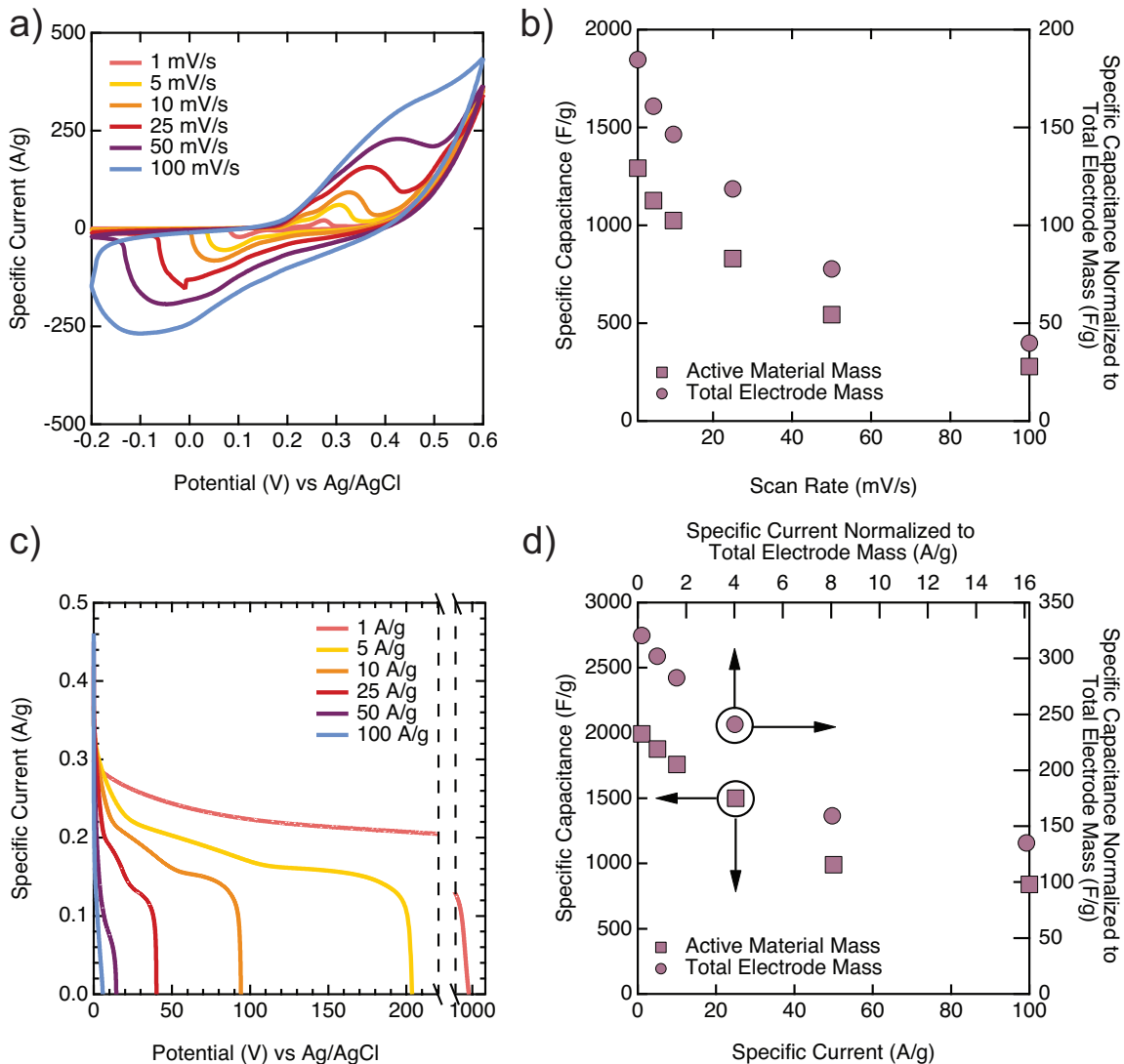
**Figure S5. Electrochemical measurements of the 8/1000 Ni/Ni(OH)<sub>2</sub> composite electrode. (a) CV curves at various scan rates; (b) gravimetric specific capacitance values as a function of scan rate; (c) galvanostatic discharge curves at various current densities; (d) gravimetric specific capacitance values as a function of current density.**



**Figure S6. Electrochemical measurements of the 15/475 Ni/Ni(OH)<sub>2</sub> composite electrode. (a) CV curves at various scan rates; (b) gravimetric specific capacitance values as a function of scan rate; (c) galvanostatic discharge curves at various current densities; (d) gravimetric specific capacitance values as a function of current density.**

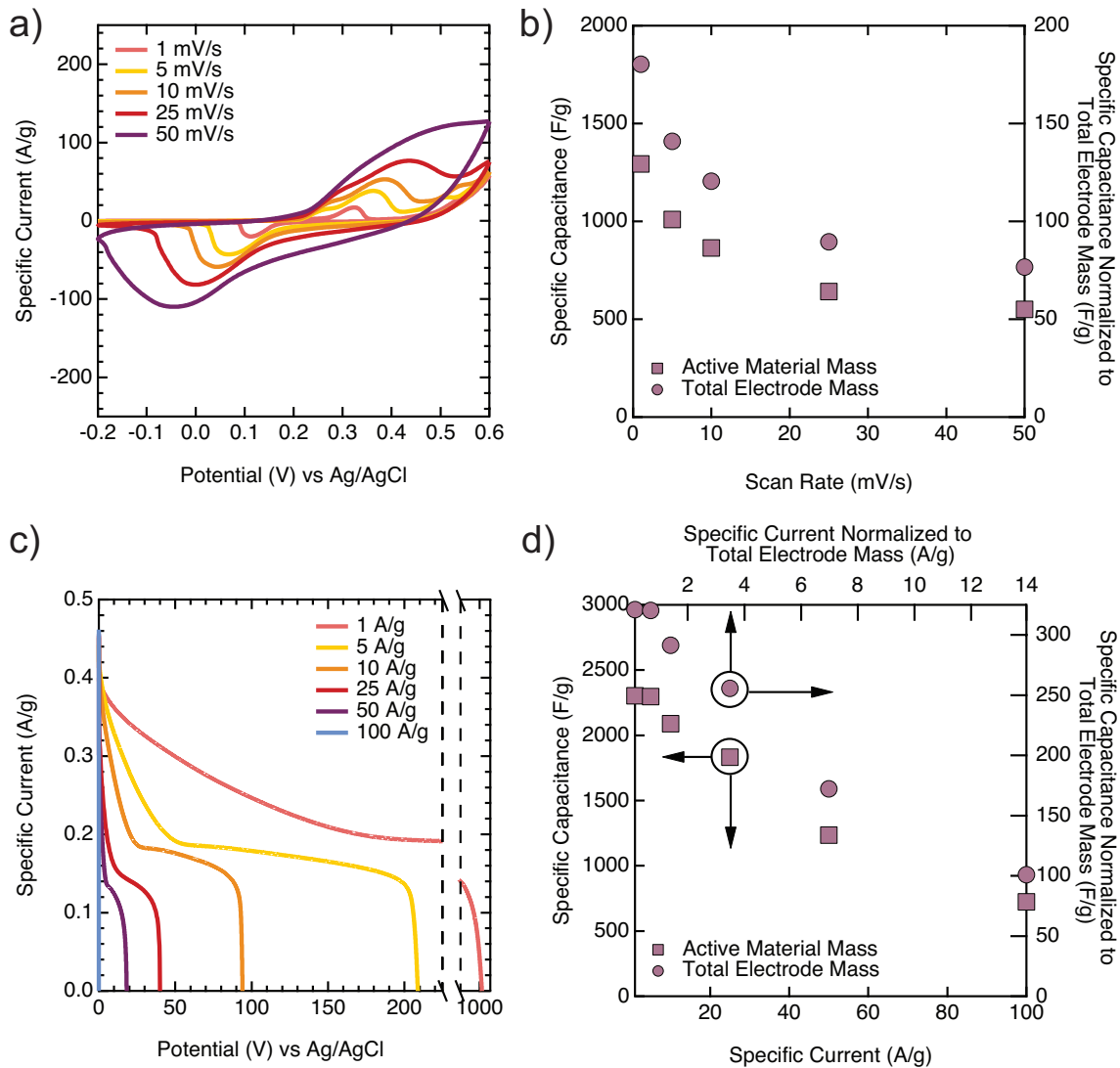


**Figure S7. Electrochemical measurements of the 15/675 Ni/Ni(OH)<sub>2</sub> composite electrode. (a) CV curves at various scan rates; (b) gravimetric specific capacitance values as a function of scan rate; (c) galvanostatic discharge curves at various current densities; (d) gravimetric specific capacitance values as a function of current density.**

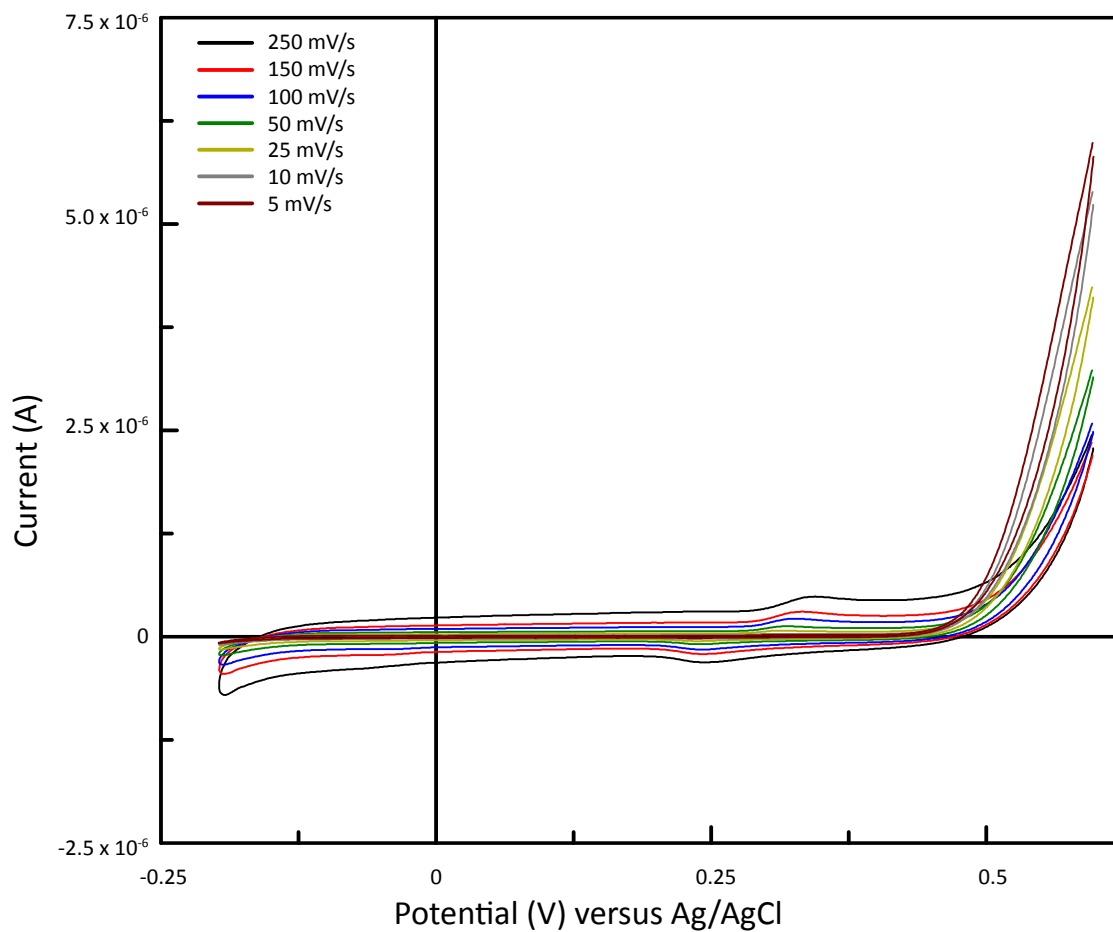


**Figure S8. Electrochemical measurements of the 15/1000 Ni/Ni(OH)<sub>2</sub> composite electrode. (a) CV curves at various scan rates; (b) gravimetric specific capacitance values as a function of scan rate; (c) galvanostatic discharge curves at various current densities; (d) gravimetric specific capacitance values as a function of current density.**





**Figure S9. Electrochemical measurements of the 22/1000 Ni/Ni(OH)<sub>2</sub> composite electrode. (a) CV curves at various scan rates; (b) gravimetric specific capacitance values as a function of scan rate; (c) galvanostatic discharge curves at various current densities; (d) gravimetric specific capacitance values as a function of current density.**



**Figure S10. CV plot of platinum mesh in 6M KOH at various scan rates, displaying the ORR reaction that occurs between the platinum and KOH. However, it is important to note the magnitude of these peaks is insignificant compared the redox peaks of nickel hydroxide. Thus even though this peak appears at high scan rates, it does not noticeably change the calculated energy and power densities or the main conclusions of this work.**

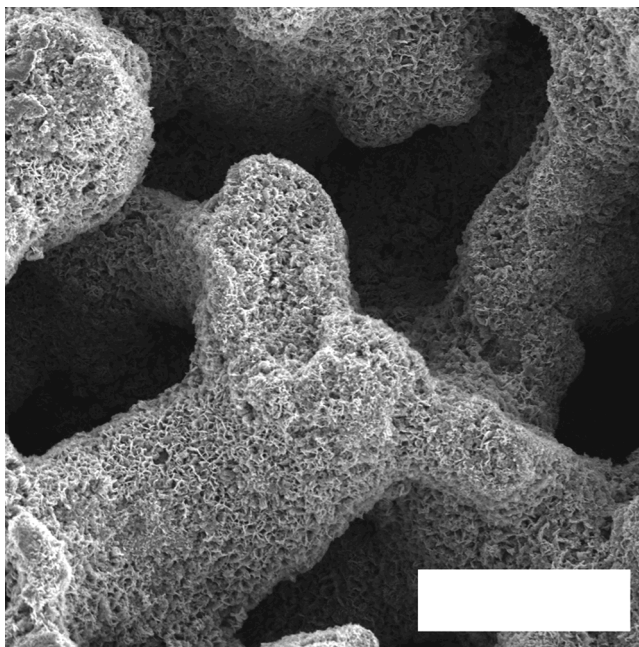


Figure S11. The 22/675 Ni/Ni(OH)<sub>2</sub> electrode after 1000 cycles at 25 A/g. The scale bar denotes 20 μm.

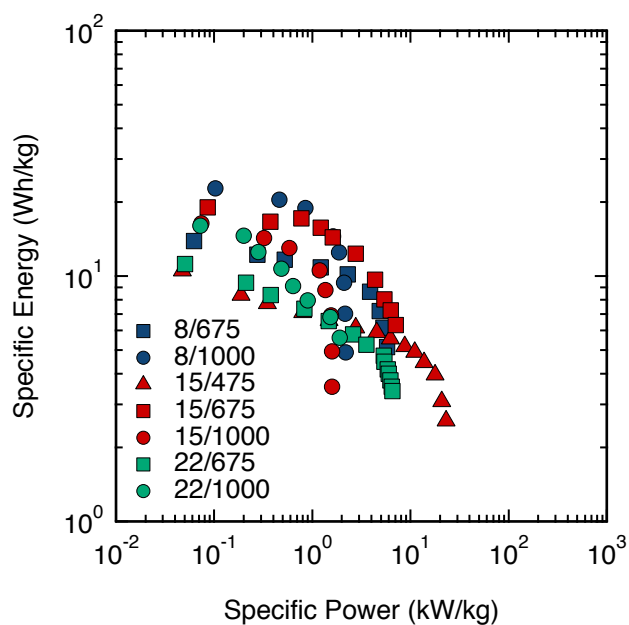


Figure S12. Gravimetric Ragone Plot. Energy and Power densities of our bijel-based Ni/Ni(OH)<sub>2</sub> electrodes based on the total mass of the electrode.

### Calculation of Energy and Power Densities

Energy densities can be calculated from the CV curves using the following equation:

$$d_e = \frac{1}{2} C_s (\Delta V)^2$$

where  $C_s$  (F/g) is the calculated specific capacitance and  $\Delta V$  (V) is the potential window.

Power densities were calculated using the following equation:

$$d_p = \frac{d_e}{\Delta t}$$

where  $d_e$  is the calculated energy density (Wh/kg) and  $\Delta t$  is the discharge time.

To estimate the performance of our electrode in a two electrode setup, the volumetric energy densities were calculated as follows:

$$d_e = \frac{1}{8} C_s (\Delta V)^2$$

and the power densities were recalculated using the equation above for power density. Theoretically the specific capacitance of a three-electrode cell is one-fourth that of a two electrode cell, thus a factor of four was introduced.

### Transient Diffusion Model

We consider the transient production and diffusion of protons through the electrolytically active material. Since  $\xi \gg L$  (note  $\xi$  is proportional to the radius of curvature in spinodal structures), we neglect curvature (see Figure S13).

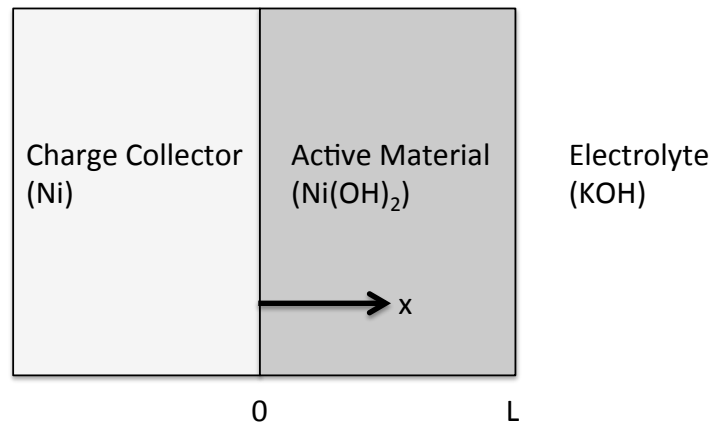


Figure S13. Schematic representation of the transport domain for the transient ion diffusion model

Recall that the redox reaction:



occurs at a constant rate within the diffusion domain, until all dissociable groups are exhausted. This will be represented by a zeroth order reaction with reaction constant  $k$  in the model. We denote the reacting species as OH (dissociable groups in Ni(OH)<sub>2</sub>) and the diffusing products (protons) as H. Assuming that the Ni phase is impermeable to protons, proton incorporation into the electrolyte occurs much more rapidly than proton diffusion through the solid phase, and the initial concentration of the dissociable groups is  $C_0$ , the governing equations and boundary and initial conditions are:

$$\frac{\partial C_H}{\partial t} = D_H \frac{\partial^2 C_H}{\partial x^2} + k$$

$$\frac{\partial C_{OH}}{\partial t} = -k$$

$$\text{BCs: } \begin{cases} \frac{\partial C_H}{\partial x}(x=0, t) = 0 \\ C_H(x=L, t) = 0 \end{cases} \quad \text{ICs: } C_H(x, t=0) = 0, \quad C_{OH}(x, t=0) = C_0$$

The second equation readily gives:  $C_{OH} = C_0 - kt$ . This in turn allows us to find the total duration of the experiment,  $t_r$ , which is the time needed for all dissociable groups to be exhausted (equivalent to the duration that a constant current can be drawn from the system). We get:

$$t_r = \frac{C_0}{k}$$

The first differential equation can now be solved for the duration  $0 < t < t_r$  using Finite Fourier Transform (FFT). The basis functions and eigenvalues are identified as:

$$\phi_n(x) = \frac{\sqrt{2}}{L} \cos(\lambda_n x), \quad \lambda_n = \left(n + \frac{1}{2}\right) \frac{\pi}{L}, \quad n = 0, 1, 2, \dots$$

And the solution through FFT is:

$$C_H(x, t) = \frac{2k}{LD_H} \sum_{n=0}^{\infty} \frac{(-1)^n}{\lambda_n^3} \cos(\lambda_n x) [1 - \exp(-\lambda_n^2 D_H t)] \quad 0 < x < L, \quad 0 < t < t_r$$

To proceed, we consider the electrochemical energy density to be proportional to the amount of protons that diffuse into the electrolyte (equivalent to the amount of dissociable groups that are successfully utilized) during the experiment. This can be calculated from the instantaneous proton flux at  $x = L$ :

$$N_H(x=L, t) = -D_H \frac{\partial C_H}{\partial x}(x=L, t) = \frac{2k}{L} \sum_{n=0}^{\infty} \frac{(-1)^{2n}}{\lambda_n^2} [1 - \exp(-\lambda_n^2 D_H t)]$$

The total amount of protons that diffuse into the electrolyte per unit active material/electrolyte interfacial area is then:

$$G = \int_0^{t_r} N_A(x=L, t) dt = \frac{2k}{L} \sum_{n=0}^{\infty} \frac{(-1)^{2n}}{\lambda_n^2} \left[ t_r + \frac{1}{D_H \lambda_n^2} (\exp(-\lambda_n^2 D_H t_r) - 1) \right]$$

To convert this expression to one of Energy Density ( $E$ ) as a function of Power Density ( $P$ ), we use:

$$t_r = \frac{C_0}{k}, \quad k = \frac{2\rho P}{nF\Delta V}, \quad E = \frac{nF\Delta VG}{2L\rho},$$

where  $n$  is the stoichiometric number of electrons involved in the reaction,  $F$  is Faraday's constant,  $\Delta V$  is the applied voltage, and  $\rho$  is the density of nickel hydroxide. Therefore,  $E$  and  $P$  are related as:

$$E = \frac{nF\Delta V}{3.6L^2\rho} \sum_{i=0}^{\infty} \left[ \frac{C_0}{\lambda_i^2} + \frac{2\rho P}{nF\Delta V D_H \lambda_i^4} \left( \exp\left(-\frac{\lambda_i^2 D_H C_0 nF\Delta V}{2\rho P}\right) - 1 \right) \right]$$

where a factor of 3.6 W.s.g<sup>-1</sup>/W.h.kg<sup>-1</sup> is also introduced for unit conversion.

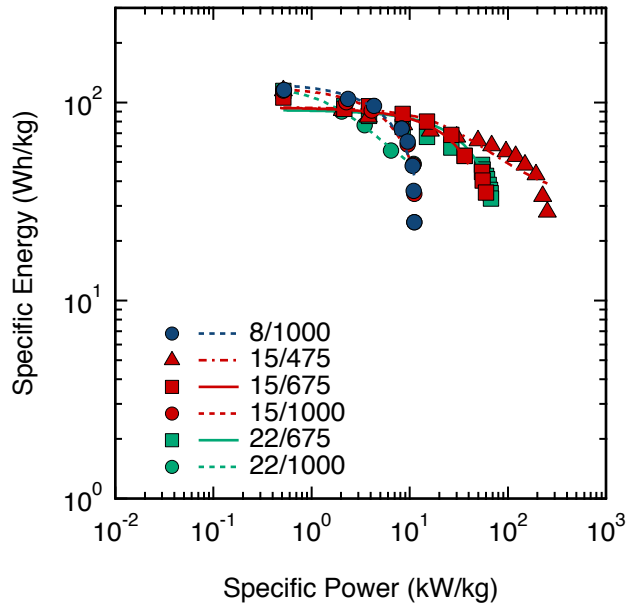


Figure S14. Model Predictions. Data for the electrodes from Fig. 4a compared with the model predictions.

**Table S2.** Extracted  $a_1$ ,  $a_2$ ,  $a_3$  and  $R^2$  values from the model predictions for each electrode.

<b>Electrode</b>	<b><math>a_1</math></b>	<b><math>a_2</math></b>	<b><math>a_3</math></b>	<b><math>R^2</math></b>
8/675	104.28	1.1171	32379	0.97143
8/1000	116.22	4.8883	567.9	0.93858
15/475	83.869	0.20435	104,750	0.88223
15/675	94.543	1.3234	32872	0.95399
15/1000	120.7	6.4007	571.16	0.93327
22/675	99.452	1.0325	32674	0.92323
22/1000	101.57	4.9913	518.59	0.91615