Supplemental Information

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Arrays Enabled by Regulated Electric Field

Distribution for Ultra-Stable Li-Metal Anodes

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Uniform Li plating/stripping within Ni macropore arrays enabled by regulated electric field distribution for ultra-stable Li-metal anodes

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TRANSPARENT METHODS

Fabrication of Ni macropore arrays

Ni macropore arrays on a Cu substrate were prepared by the electrochemical deposition method(Li et al., 2007; Zhang et al., 2012). Prior to use, a piece of Cu foil was thoroughly rinsed with acetone, ethanol and deionized water in sequence. Then the Cu foil was masked by the insulating Kapton film, leaving an exposed area of 2.25 cm^2 (1.5 cm × 1.5 cm). The treated Cu foil and carbon paper (4.0 cm × 5.0 cm) were used as the working electrode and counter electrode, respectively. The electrolyte was 2.0 M NH_4Cl and 0.1 M $NiCl_2 \cdot 6H_2O$ aqueous solution. The electrodeposition process was performed at a constant current density of 3.0 A cm^{-2} for the duration of 60 seconds with vigorous stirring. The resulting brown films on the Cu foil were immersed in 500 mL deionized water to remove the residual electrolyte, and dried overnight at 60 °C in the vacuum oven.

Characterizations

X-ray diffraction (XRD) patterns were recorded on the Miniflex 600 diffractormeter (Rigaku) with Cu Kα radiation. The morphology of samples was characterized by using a scanning electron microscope (SEM, S-3400N, Hitachi). Prior to the analyses, the electrodes after cycling were disassembled from the electrochemical cells, rinsed three times with DME (1,2-dimethoxyethane) solvent, and dried in the grove box.

Numerical simulation

The model is constructed in COMSOL Multiphysics framework. In order to simulate the deposition process which involves large shape distortion, the level set method is chosen to

track the moving boundary of lithium metal surface. General PDE module is used to describe the electrochemical system.

Level set method use a status variable ξ to distinguish different phases. ξ equals to 0 and 1 in solid and liquid phases respectively. The following equation is solved to track the moving interphase:

$$\frac{\partial \xi}{\partial t} + \boldsymbol{u} \cdot \nabla \xi = \gamma \nabla \cdot (\epsilon \nabla \xi - \xi(1 - \xi)\frac{\nabla \xi}{|\nabla \xi|})$$

γ determines the amount of initialization. ϵ determines the thickness of transition region. $\boldsymbol{u}$ is the velocity field which is related to local current density through molar volume of lithium metal:

$$\boldsymbol{u} = \frac{i_{loc} V_m}{F} \cdot \frac{\nabla \xi}{|\nabla \xi|}$$

F is Faraday's constant. $\frac{\nabla \xi}{|\nabla \xi|}$ is the normal vector at the interphase. The molar volume V_m is 12.998 cm^3 mol^{-1}.

The current density in liquid and solid phase are described by following equations:

$$i_l = -\sigma_{l,eff}\nabla\phi_l + \left(\frac{2\sigma_{l,eff}RT}{F}\right)\left(1 + \frac{\partial lnf}{\partial lnc_l}\right)(1 - t_+)\nabla lnc_l$$

$$i_s = -\sigma_{s,eff}\nabla\phi_s$$

Here $\frac{\partial lnf}{\partial lnc_l} = \left(0.601 - 0.24c_l^{0.5} + 0.893(1 - 0.0052(T - 294))c_l^{1.5}\right)(1 - t_+^0)^{-1} - 1$ accounts for the activity dependence. The transfer coefficient t_+=0.38. In order to combine PDEs with level set method, statistic electro potential in both phases has to be continuous in the whole model. Thus, the electronic conductivities are modified by status function ξ as $\sigma_{l,eff} = \sigma_l\xi + \sigma_0(1 - \xi)$ and $\sigma_{s,eff} = \sigma_0\xi + \sigma_s(1 - \xi)$. σ_0 is set to 1×10^{-8} S m^{-1}.

The controlling equations of charge conservation in both phases are written as followings:

$$\nabla \cdot i_l = i_{loc}\delta$$

$$\nabla \cdot i_s = -i_{loc}\delta$$

Here, $\delta = 6\xi(1-\xi)\left|\frac{\nabla\xi}{|\nabla\xi|}\right|$ is a function whose integration over 0 to 1 is 1 and is nonzero only in the interphase region. Local current density arising from overpotential η is defined by Butler-Volmer equation herein as:

$$i_{loc} = Fkc_l^{0.5}\left(exp\left(\frac{0.5F\eta}{RT}\right) - exp\left(-\frac{0.5F\eta}{RT}\right)\right)$$

$k=1.147\times10^{-4}$ mol m^{-2} s^{-1} is the reaction rate constant.

The mass conservation in liquid phase is given by:

$$\xi\frac{\partial c_l}{\partial t} - D_l c_l + \frac{i_l t_+}{F} = \frac{i_{loc}\delta}{F}$$

In which the electrolyte diffusivity $D_l = 10^{-4} \times 10^{-4.43 - \frac{54}{T-229-5c_l} - 0.22c_l}$ (Sturm et al., 2019).

Electrochemical measurements

Electrochemical measurements were performed by using CR-2016 type coin cells. The Ni macropore array electrode was punched into discs with the diameter of 1.2 cm, and used as the working electrode. A metallic Li foil with the diameter of 1.6 cm was used as the reference and counter electrode. Lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI, 1.0 M) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (volume ratio = 1/1) with 1 wt% LiNO$_3$ as additive was used as the electrolyte, and the amount of electrolyte used in the assembly of half cells was fixed at 0.089 mL mAh^{-1} when the Li plating capacity was

1 mAh cm^{-2}. Celgard 2400 microporous polypropylene membrane was employed as the separator. Before Li plating, the half cells were primarily activated for 5 cycles at 0.5 mA cm^{-2} between 0 and 1.0 V (vs. Li$^+$/Li) to stabilize SEI and remove surface contaminations. For the test of CEs, the plating process was set to a certain area capacity at a constant area current density, and the stripping process was charging to 1.0 V. For the fabrication of symmetric batteries, 4.0 mAh cm^{-2} of Li was predeposited onto the Ni macropore array electrodes, and two as-prepared electrodes were assembled together into the CR-2032 type coin cells. Then a fixed capacity of 1 mAh cm^{-2} was applied during repeated discharge/charge at 0.5 mA cm^{-2} to obtain the time-voltage profiles. Electrochemical impedance spectroscopy (EIS) was collected with the frequency range of 100 kHz ~ 0.1 Hz by using the electrochemical workstation (Interface 1010B, Gamry).

The full cells were assembled by using 4 mAh cm^{-2} of deposited Li on Ni macropore array electrode as the anode, and LiFePO$_4$ electrode as the cathode. For the preparation of LiFePO$_4$ electrode, 80 wt% commercial LiFePO$_4$ (Hefei Guoxuan High-tech Power Energy Co., Ltd), 10 wt% super P and 10 wt% PVDF (polyvinylidene fluoride) was thoroughly mixed in NMP (N-methylpyrrolidine) solvent. The slurry was coated onto the Al foil by using an automatic film coating machine, and dried a vacuum oven at 80 °C for 12 h. The mass loading of active materials in LiFePO$_4$ electrodes is approximately 4.3 ~ 4.8 mg cm^{-2}. All the electrochemical properties were measured at the room temperature.
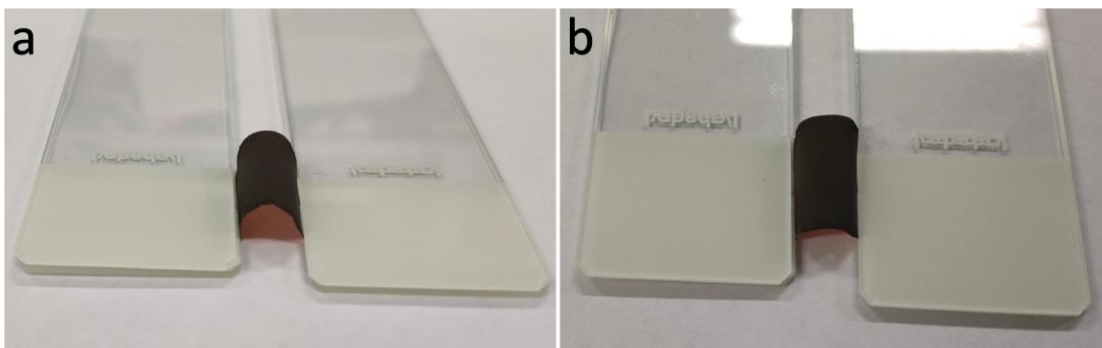
Figure S1. Photographs of the bending test of the Ni macropore array electrode. Related to
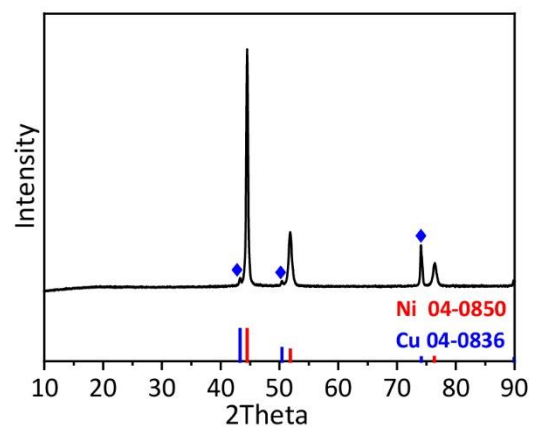
Figure 1.

Figure S2. XRD patterns of the Ni macropore array electrode. Related to Figure 1.

Table S1. The comparison of graphite and Li-Ni macropore array anode in terms of gravimetric specific capacity and volumetric specific capacity. The specific discharge capacity of commercial graphite (Alladin) was evaluated to be ~334.7 mAh g^{-1} at 0.5 C, and the tap density was measured to be approximately 0.71 g cm^{-3}. Related to Figure 1.

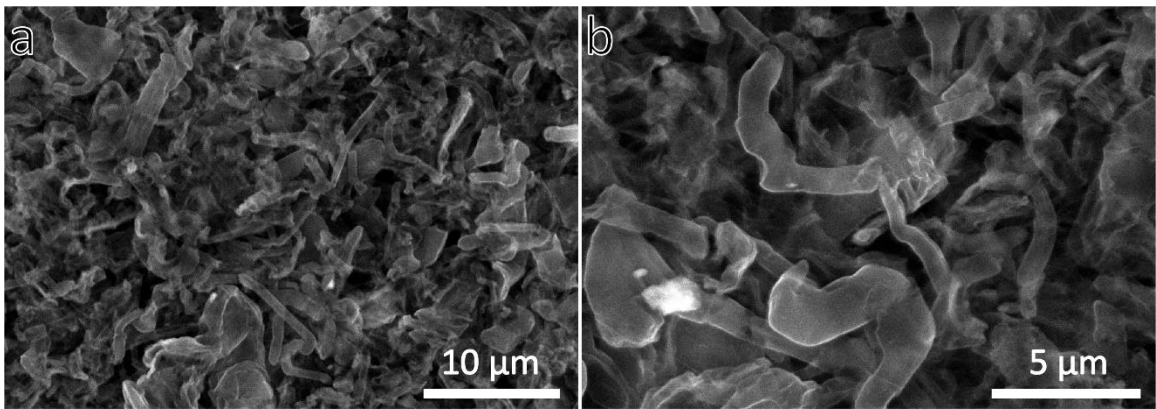| Sample	Gravimetric specific capacity (mAh g^{-1})	Volumetric specific capacity (mAh cm^{-3})
Graphite	334.7	237.6
Li-Ni macropore array anode	537.6	1010.1

Figure S3. SEM images of the Cu foil electrode after discharging to 1.0 mAh cm^{-2} at 0.5 mA cm^{-2}. Related to Figure 2.
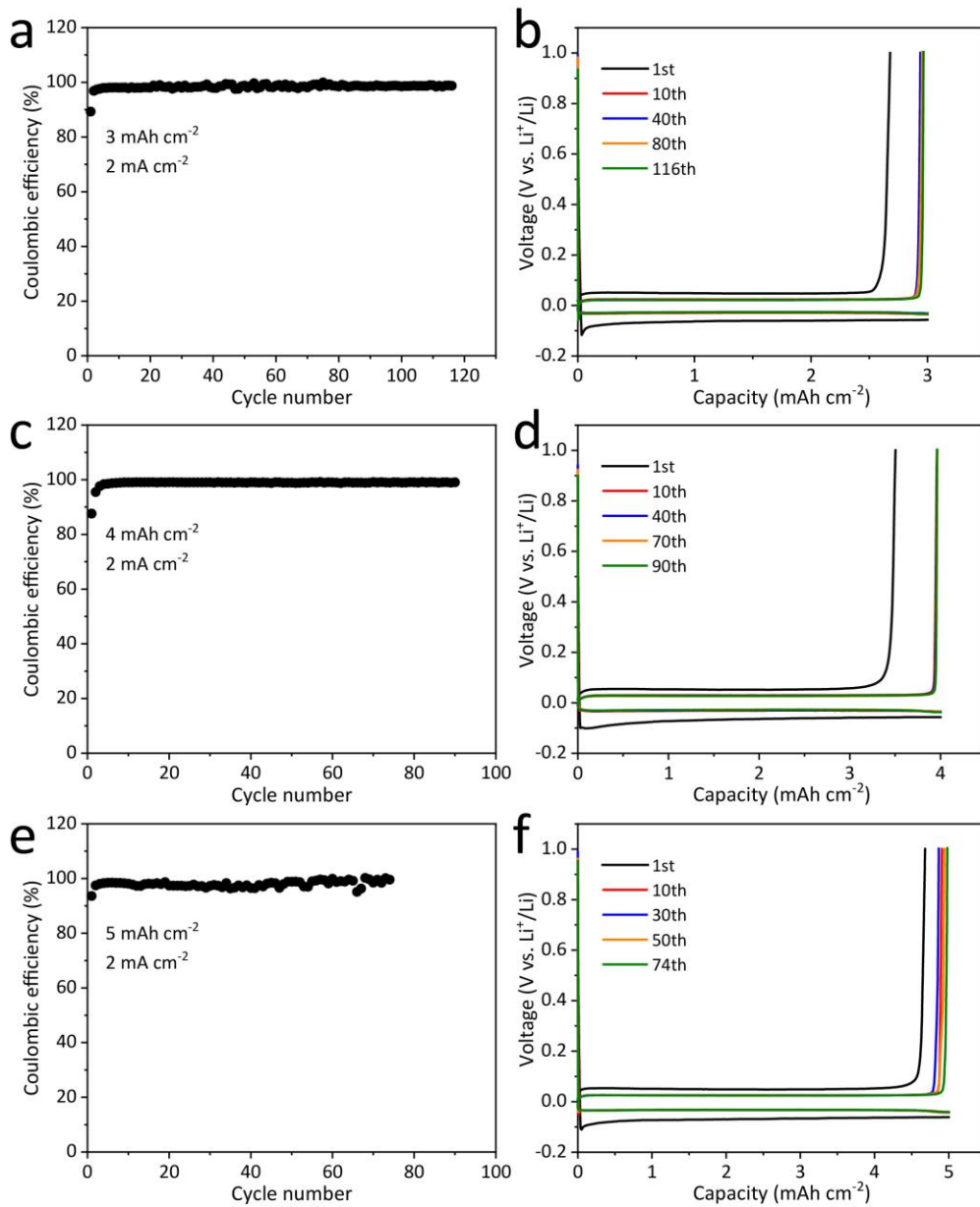
Figure S4. Coulombic efficiency evaluation and voltage profiles of the Li plating/stripping process on the Ni macropore array electrode measured at 2 mA cm^{-2} for (a, b) 3 mAh cm^{-2}, (c, d) 4 mAh cm^{-2} and (e, f) 5 mAh cm^{-2}. The amounts of electrolyte used in the assembly of half cells cycling at various capacities were 0.029, 0.022 and 0.018 mL mAh^{-1}

corresponding to the cycling capacities of 3, 4 and 5 mAh cm^{-2}, respectively. Related to
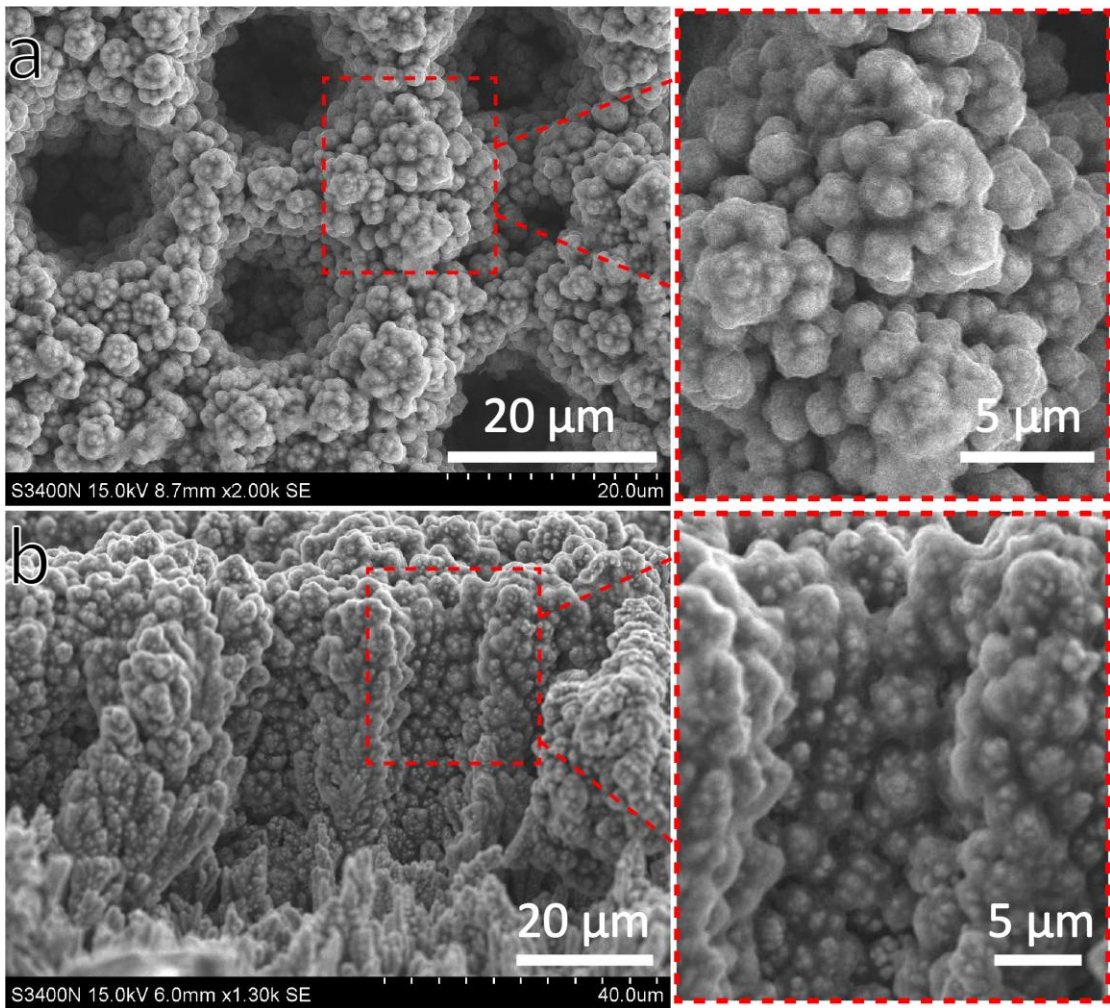
Figure 3.

Figure S5. (a) The surface SEM image and (b) the cross-sectional SEM image of the Ni macropore array electrode after 50 cycles. Related to Figure 4.
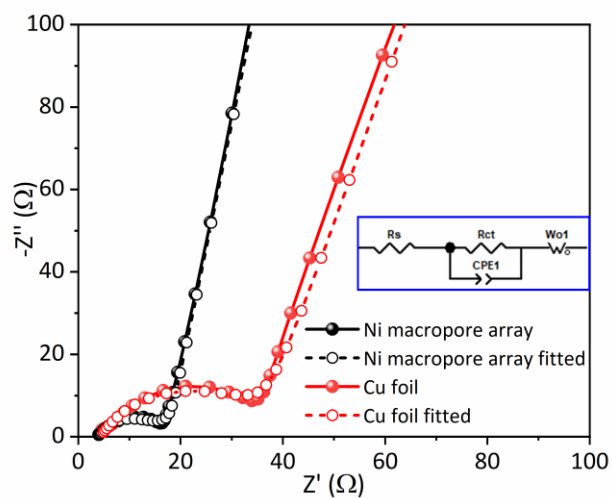
Figure S6. EIS and fitting results of the Ni macropore array and Cu foil electrodes after 100 cycles (inset is the equivalent circuit model). Related to Figure 4.

Table S2. Equivalent-circuit parameters obtained by fitting the experimental impedance spectra. Related to Figure 4.

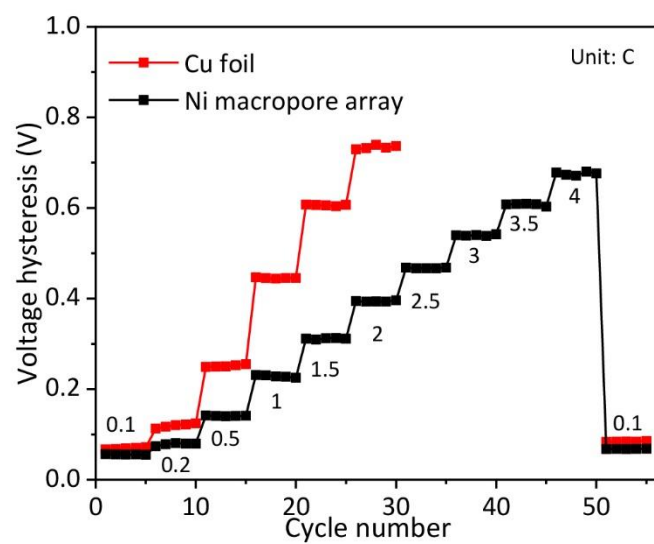| Sample	R_s (Ω)	Error	R_{ct} (Ω)	Error
Cu foil	4.06	3.43%	22.7	3.25%
Ni macropore array	3.80	1.49%	9.06	2.00%

Figure S7. Voltage hysteresis of full cells with Li-Ni macropore array anode and Li-Cu foil anode against LiFePO₄ cathode. Related to Figure 5.

Supplemental Reference

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