Supporting Information

A Hierarchical Three-dimensional $NiCo_2O_4$ Nanowire Arrays/Carbon Cloth as Air Electrode for Nonaqueous Li-air Batteries

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Cell assembly

The assembly of the cell has been described in detail in our recent work [Y. Yang, Q. Sun, Y. S. Li, H. Li, Z. W. Fu. J. Electrochem. Soc. 158 (2011) B1211]. The model cell consisted of an H shape glass tube to separate positive and negative electrodes as well as two rubber plugs for sealing. The cell was constructed with the NCONW/CC as the cathode and one sheet of high-purity lithium foil as the anode, respectively. The electrolyte was 1.0 M Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,2-dimethoxyethane (DME). The discharge and charge processes were performed at room temperature with a Land BT 1-40 battery test system. When the cells were cycled in the containers, the dried air diffused into the electrolyte solution spontaneously and supported the cycling of the cells. The current densities and capacities of electrodes were calculated based on the weight of $NiCo_2O_4$ nanowires.

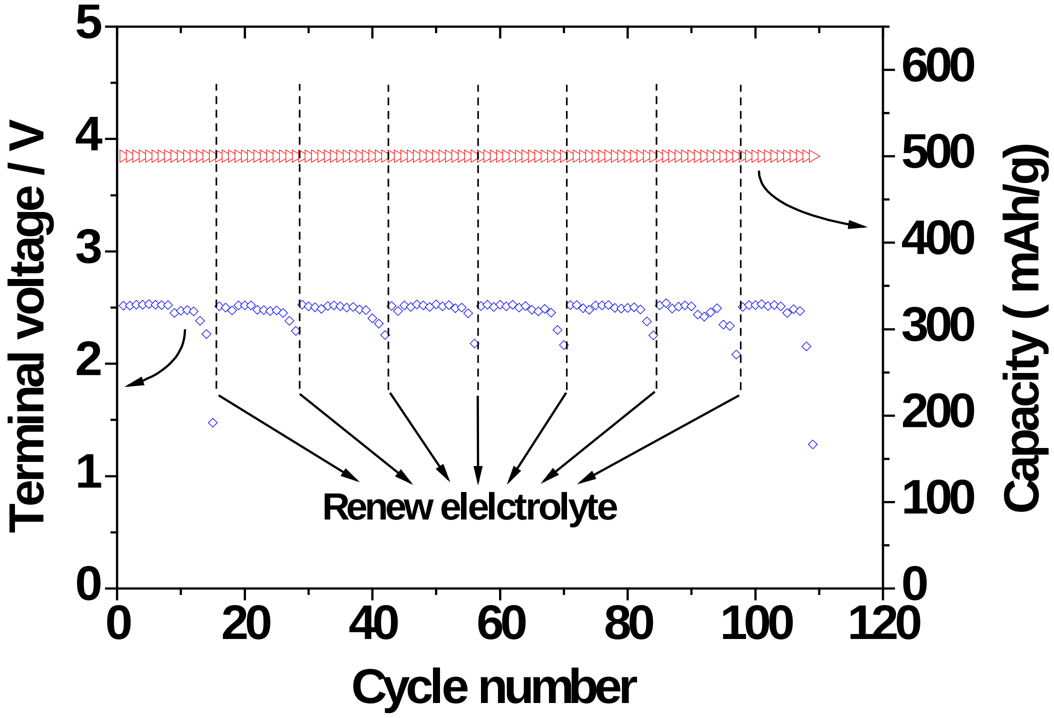

Figure S1 Voltage of the terminal discharge vs. the cycle number for Li-air battery with $NiCo_2O_4$ nanowire catalyst at 80 mA g^{-1}. The electrolyte was renewed by driving out the plug, pouring out the deteriorated electrolyte, and injecting with new electrolyte, when the terminal voltage of discharge was decreased obviously. After renewing the electrolyte, the performance of cycling capability and capacity, discharge/charge voltage platform, and terminal voltage of discharge are thoroughly recovered as a new battery.

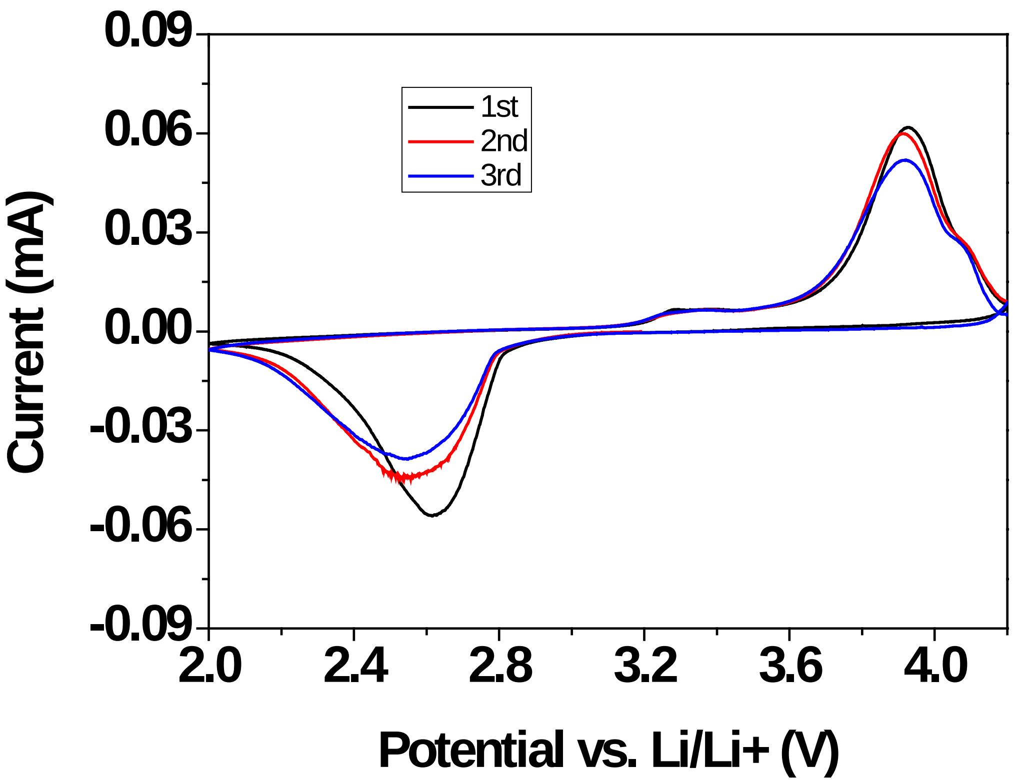

Figure S2 The initial three cycle profiles of cyclic voltammograms for NCONW/CC in aqueous electrolyte (1.0 M LiTFSI in DME) with 0.02 mV s^{-1} sweep rate.

Table S1 d-spacings (Å) derived from SAED analysis of before discharge, first discharged to 2.0 V and first charged to 4.2 V of $NiCo_2O_4$ nanowire arrays/carbon cloth electrodes. JCPDS standards for $NiCo_2O_4$ and Li_2O_2 are shown for reference.

Before discharge		First discharge to 2V				First charge to 4.2V	
$NiCo_2O_4$ Fd-3m(2-1074)		Li_2O_2 P-6(9-355)		$NiCo_2O_4$ Fd-3m(2-1074)		$NiCo_2O_4$ Fd-3m(2-1074)	
T.W.[a]	Reference	T.W.	Reference	T.W.	Reference	T.W.	Reference
2.88	2.87(220)	1.57	1.57(110)	2.87	2.87(220)	2.85	2.87(220)
2.45	2.45(311)	1.47	1.45(112)	2.45	2.45(311)	2.44	2.45(311)
2.03	2.03(400)	1.20	1.20(203)	2.05	2.03(400)	2.02	2.03(400)
1.56	1.56(511)	1.03	1.03(210)			1.55	1.56 (511)
1.44	1.44(440)	a= 3.15±0.03	a=3.14			1.44	1.44 (440)
a=8.13±0.02	a=8.13	c= 7.67±0.07	c=7.65	a=8.15±0.04	a=8.13	a=8.09±0.05	a=8.13

a T.W.: this work.

Support 1: The charge density of the tip

In order to explain the charge accumulation near the tip of our conductance (the conductivity of $NiCo_2O_4$: 0.6~62 S cm^{-1} (Y. Fujishiro, K. Hamamoto, O. Shino, S. katayama, M. Awano, J. Mater. Sci. 2004, **15**, 769; L. Hu, L. Wu, M. Liao, X. Hu, X. Fang, Adv. Fun. Mater. 2012, **22**, 998) , we will consider the conductance as a cone with a small apex angle of $2\theta_0$, as showed in Figure S2 and analyze the electric potential and magnitude field around the tip of the cone.

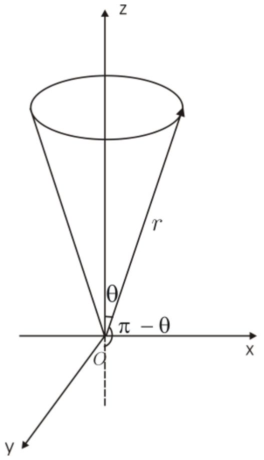

Figure *S2* The model of the cone conductance

Applying voltage of V_0 into the conductance, the charge will distribute on its surface and the magnitude of the electric field inside the conductance is zero because of electrostatic equilibrium. Because of the axial symmetry of the cone, we can choose spherical coordinates to construct our model, and the sharpness of our object asks θ to be small. We first try to find out the electric potential around the tip in the area of $2(\pi-\theta)$, where the potential satisfies the Laplace equation $\Delta\varphi(r,\theta,\phi)=0$. In the spherical coordinates, it can be write as:

$$\frac{1}{\mathrm{r}^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\varphi}{\partial r}\right)+\frac{1}{\mathrm{r}^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\varphi}{\partial\theta}\right)+\frac{1}{\mathrm{r}^2\sin^2\theta}\frac{\partial^2\varphi}{\partial\phi^2}=0 \qquad (1)$$

The axial symmetry asks φ to be independent of ϕ and with the method of separation of variables, we rewrite the potential into $\varphi(r,\theta)=R(r)\Theta(\theta)$, the Eq.(1) can be write into

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-l(l+1)R=0 \tag{2}$$

and $$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)\Theta=0 \tag{3}$$

Using the solutions of Eq.(2) and Eq.(3), we obtain the expression of potential as $\varphi(r,\theta)=\sum_l\left(A_l r^l+B_l r^{-(l+1)}\right)P_l(\cos\theta)+C_0$, where A_l, B_l and C_0 are undetermined constants and $P_l(\cos\theta)$ is Legendre function of order l with the variable $\cos\theta$, which is the solution of Eq.(3). The boundary condition asks the potential to be finite around the tip, which means $\varphi(r,\theta)\neq\infty$ when $r\to 0$, so the constant B_l should be zero. Thus the potential can be rewrite as:

$$\varphi(r,\theta)=\sum_l A_l r^l P_l(\cos\theta)+C_0 \tag{4}$$

As we will concentrate on the situation of $r\to 0$, we can leave out the high order of expression (4), keeping the lowest order, i.e. $\varphi(r,\theta)=A_l r^l P_l(\cos\theta)+C_0$, where $l<<1$. The conductance we are interested in is sharp, so in our consideration, $P_l(\cos\theta)$ is almost independent of θ, then we can rewrite Legendre function into $P_l(\cos\theta)=C(1+f(\theta))$, which should satisfy Eq.(3). More calculation will lead to $f(\theta)=l\ln(\sin\theta)+C_1\ln\left(\tan\frac{\theta}{2}\right)+C_2$,i.e.

$$f(\theta)=l\ln 2+l\ln\left(\sin\frac{\theta}{2}\right)+l\ln\left(\cos\frac{\theta}{2}\right)+C_1\ln\left(\sin\frac{\theta}{2}\right)-C_1\ln\left(\cos\frac{\theta}{2}\right)+C_2 \tag{5}$$

where $\theta\in[\theta_0,\pi]$, which asks $C_1=l$. Choose appropriate C_2 to obtain $f(\theta)=2l\ln\left(\sin\frac{\theta}{2}\right)$, then $\varphi(r,\theta)=Ar^l\left(1+2l\ln\left(\sin\frac{\theta}{2}\right)\right)+C_0$, where A is undetermined constant in our calculation. Taking the boundary condition $\varphi(\theta_0)=V_0$ into account, we can obtain $C_0=V_0$, $l=\left(2\ln(2/\theta_0)\right)^{-1}$, the final expression of potential around the tip is:

$$\varphi(r,\theta)=Ar^l\left(1+2l\ln\left(\sin\frac{\theta}{2}\right)\right)+V_0 \tag{6}$$

The magnitude of electric field could then be obtained as

$$E_r = \left| -\frac{\partial \varphi}{\partial r} \right| = Alr^l \left(1 + 2l \ln\left(\sin\frac{\theta}{2} \right) \right) \qquad (7)$$

$$E_\theta = \left| -\frac{1}{r}\frac{\partial \varphi}{\partial \theta} \right| = Alr^{l-1} \cot\left(\frac{\theta}{2} \right) \qquad (8)$$

According to Gauss theorem, the surface charge density is $\sigma = \varepsilon_0 E_\theta = \varepsilon_0 Alr^{l-1}\cot\left(\frac{\theta}{2}\right)$. On the surface of the cone $\sigma(\theta_0) = A_0 r^{l-1}$, where $l = (2\ln(2/\theta_0))^{-1}$ and A_0 is constant quantity relating to dielectric constant ε_0. The surface charge density around the tip for cones with half-apex angle of $\theta_0 = 1^o$ and $\theta_0 = 5^o$ could be analyzed from the expression (8) above and the result is shown in Figure S2. It can be clearly seen that the charge density would decrease dramatically far from the tip, i.e. there will be a huge number of charge assemble around the tip of the conductance.

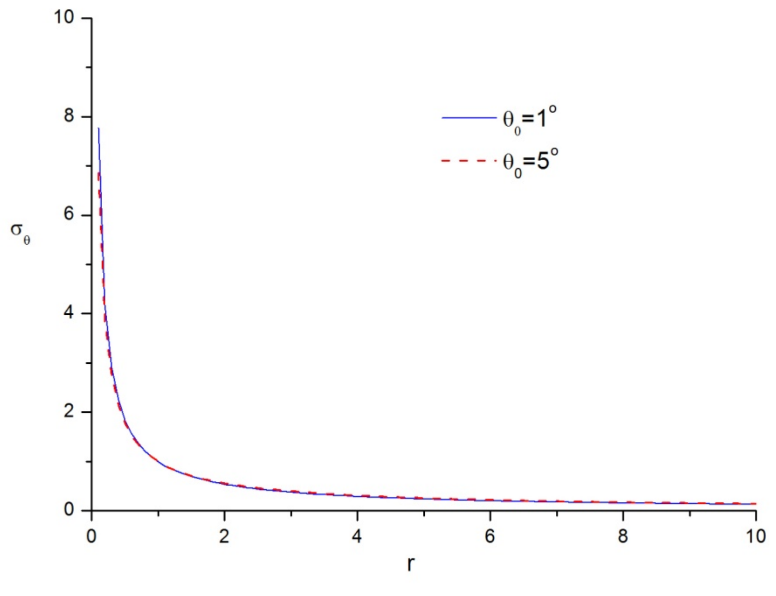

Figure *S3* The surface charge density around the tip for cones with half-apex angle of $\theta_0 = 1^o$ and $\theta_0 = 5^o$, where A_0 has been set as unit to simplify our analysis.