Supplementary Information:

Alkaline Rechargeable Ni/Co Batteries: Cobalt Hydroxides as Negative Electrode Materials

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Experimental section:

Single-crystal hexagonal platelets of β-$Co(OH)_2$ were prepared in a beaker starting from a dilute aqueous solution of $CoCl_2$•$6H_2O$ and hexamethylene tetramine (HMT) under ambient atmosphere as described in a previous reference.[1] The structure of the sample was characterized by X-ray diffraction (XRD, Rigaku D/max-2500) using CuKα radiation. The morphology was investigated with scanning electron microscope (SEM, Hitachi S-3500N).

The electrochemical measurements were carried out in a three-compartment cell. A sintered nickel electrode with a large capacity and an Hg/HgO electrode in 6 M KOH solution were served as counter and reference electrodes, respectively. Electrodes used for tests were constructed by mixing the as-prepared cobalt hydroxide with carbonyl nickel powder (NICO 255) in a weight ratio of 1:3. The mixture powder was pressed under 30 MPa into a small pellet of 10 mm in diameter and 1.5 mm in thickness. The rate capability tests of this material were performed using Land battery test instruments controlled by a computer. The negative electrodes were charged at 1, 2, 5 and 10 C rate for 1.5, 0.75, 0.3 and 0.15 h, respectively, and then discharged at the same rate to −0.6 V (vs Hg/HgO). Cyclic voltammetry (CV) experiments were conducted using Zahner IM6e electrochemical workstation. The working electrodes for CV tests were made by mixing active materials with polytetrafluoroethylene (PTFE) aqueous suspension, pasting the mixture into

nickel foam and then drying in vacuum before testing. The scan rate of CV measurement was set to be 0.2, 0.4, 0.6, 0.8 and 1 mV/s in the potential range of −0.4~ −1.2 V (vs Hg/HgO).

To confirm the electrochemical reaction mechanism, the structure of the β-$Co(OH)_2$ particles, after charging/discharging process, was measured by XRD. In order to avoid the influence of the Ni diffraction peaks, the electrodes for XRD measurements were prepared by mixing β-cobalt hydroxides, acetylene black and polytetrafluoroethylene (PTFE) at the weight ratio of 10:2:1 into a paste, which was roll pressed to a film of 0.15 mm in thickness and then pressed onto a porous nickel mesh. After the charging/discharging process, the sample was washed with distilled water and ethanol, and dried in vacuum.

The output energy of the alkaline rechargeable battery fabricated by Al-substituted α-$Ni(OH)_2$ (as prepared in our previous work[2]) and β-$Co(OH)_2$ was measured. The Al-substituted α-$Ni(OH)_2$, cobalt oxide powders, and Ni powders were mixed with a weight ratio of 65.6:7.7:26.7. A 1.0 wt% binder (hydroxypropyl methylcellulose, HPMC) was added to the mixture to obtain a paste, which was incorporated into nickel foam (2.0 cm × 2.0 cm). The obtained nickel electrodes were dried at 50 ℃ and then pressed under 30 MPa. The electrode was subsequently soaked in 6 M KOH for 24h before using. Then, the resultant positive electrode was coupled with β-$Co(OH)_2$ negative electrode. The Ni/Co cell was charged and discharged at room temperature with 1.0 C rate, and the cut-off voltage was 0.8V.

References

1) Z. P. Liu, R. Z. Ma, M. Osada, K. Takada, T. Sasaki, *J. Am. Chem. Soc*. **2005**, 127, 13869.
2) Q. D. Wu, X. P. Gao, G. R. Li, G. L. Pan, T. Y. Yan, H. Y. Zhu, *J. Phys. Chem. C* **2007**, 111, 17082.

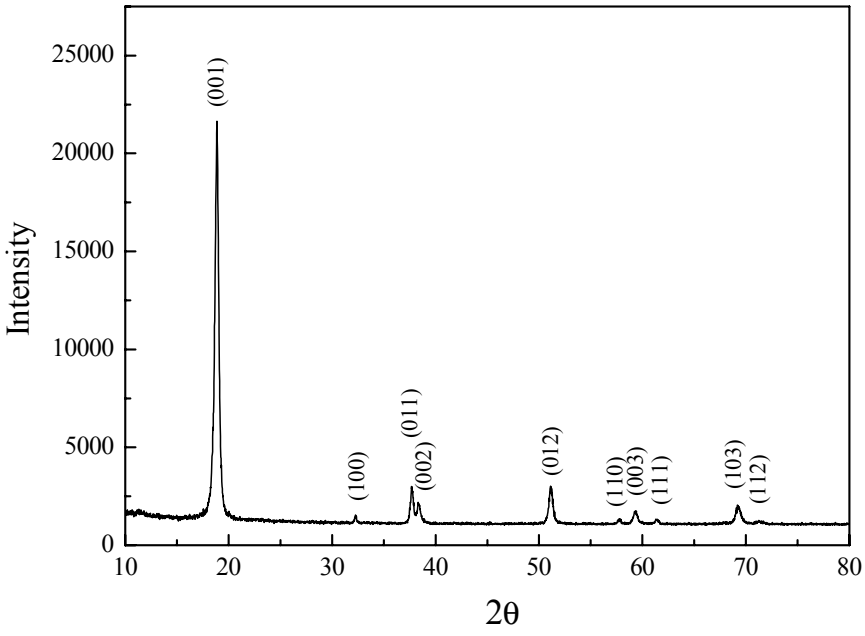

Figure S1. XRD pattern of as-prepared β-$Co(OH)_2$ particles

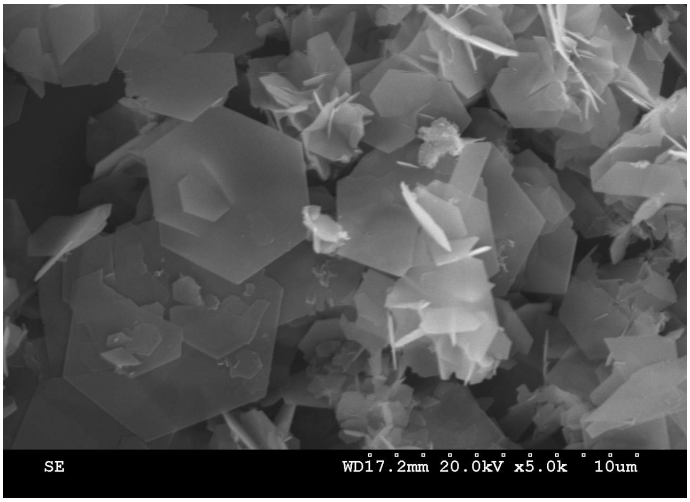

Figure S2. SEM image of as-prepared β-$Co(OH)_2$ particles

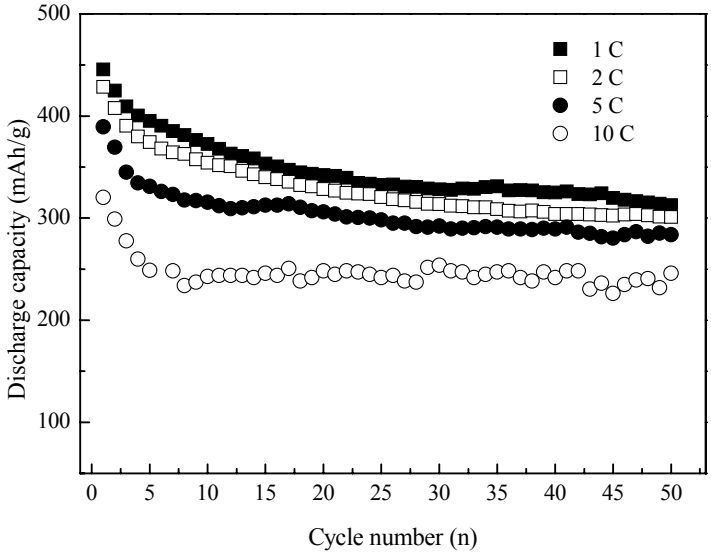

Figure S3. Cycle performance of α-$Co(OH)_2$ electrodes at different discharge rates

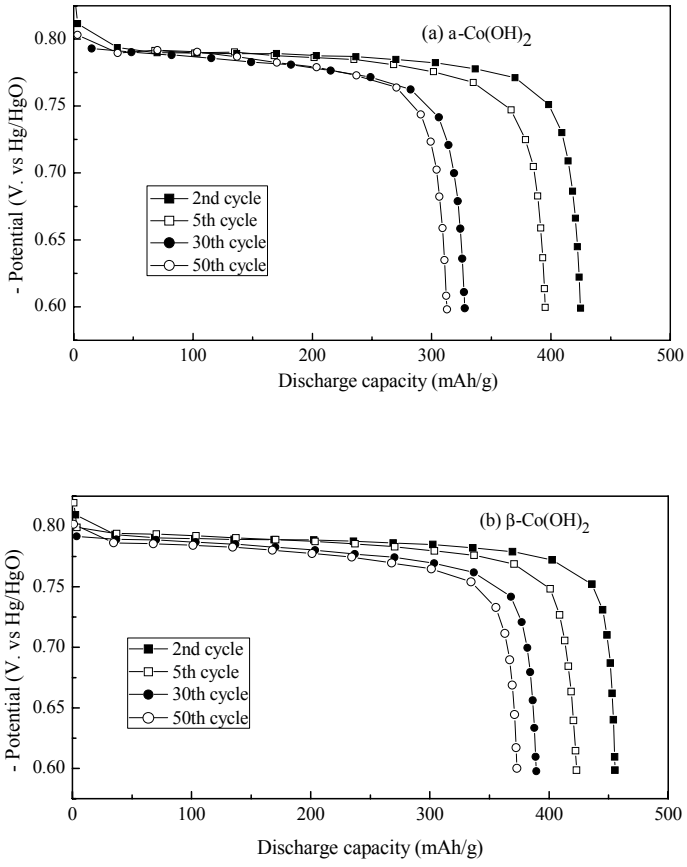

Figure S4. Discharge curves of both β-$Co(OH)_2$ and α-$Co(OH)_2$ electrodes at different cycles at 1C rate

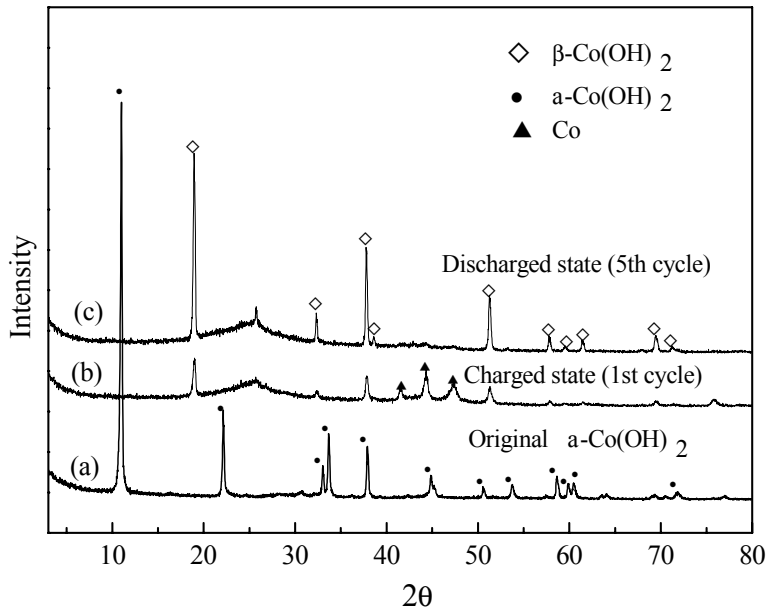

Figure S5. XRD patterns of α-$Co(OH)_2$ at different charge/discharge state

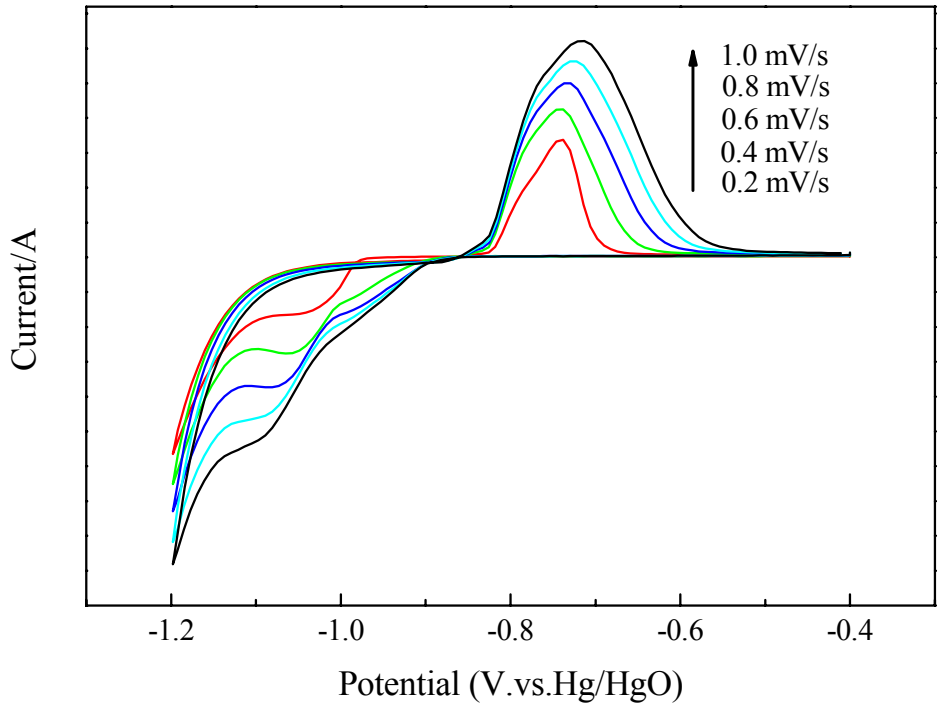

Figure S6. Cyclic voltammograms (CVs) of β-$Co(OH)_2$ electrode at different scan rates

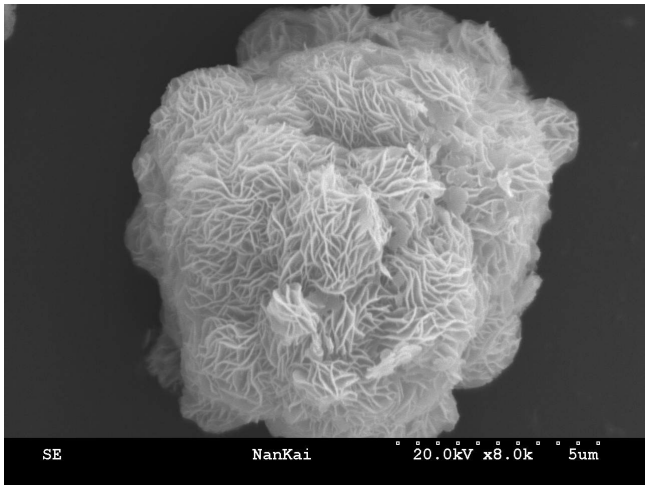

Figure S7. SEM image of as-prepared α-$Ni(OH)_2$ microspheres

Table S1. The main feature of the different alkaline secondary batteries

Battery systems	Negative electrode	Specific energy (Wh/kg)	Environmental impact
Ni/Cd (commercial)	Cd	30~50	toxic
Ni/MH (commercial)	Metal hydrides	70~90	green
Ni/Co (prototype)	$Co(OH)_2$	~160	green