

Electronic Supplementary Information

Porous NiCo₂O₄ as anode materials for 4.5 V hybrid Li-ion capacitors

Rui Ding,^{*a,b} Li Qi^a and Hongyu Wang^a

^a State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China

^b Graduate University of Chinese Academy of Sciences, Beijing 100039, China

* Email: dingrui@ciac.jl.cn

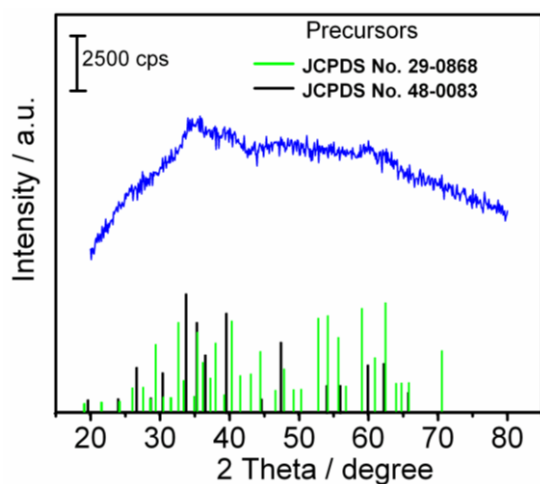


Fig. S1 XRD patterns of as-synthesized precursors.

Fig. S1 shows the XRD patterns of precursors. The precursors are identified as typical nickel-cobalt hydroxide carbonate compound composed of $\text{NiCO}_3(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (JCPDS No. 29-0868) and $\text{Co}(\text{CO}_3)_{0.5}(\text{OH}) \cdot 0.11\text{H}_2\text{O}$ (JCPDS No. 48-0083), which corroborate with the precursors for the reported pure spinel NiCo_2O_4 prepared from chemical co-deposition method for supercapacitors.^{1,2}

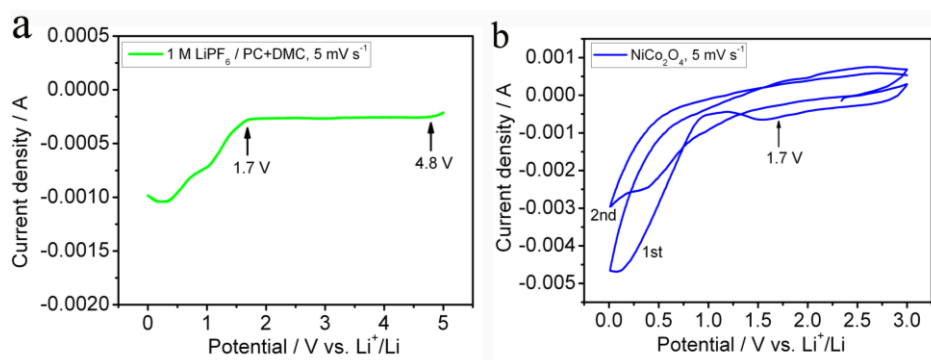
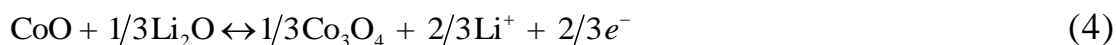
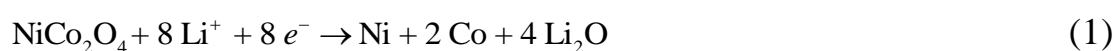


Fig. S2 (a) LSV plots of 1 M LiPF₆ (PC+DMC, 1:1 in volume) at 5 mV s⁻¹ and (b) CV plots of the first two cycles of NiCo₂O₄ electrode at 5 mV s⁻¹.

Fig. S2a shows LSV plots of the electrolytes at 5 mV s⁻¹. The oxidation potential is known to exceed 4.8 V (vs. Li⁺/Li), which is larger than the upper-limit potential of positive electrode (4.5 V), and therefore the electrolytes can't decompose by oxidation, while the electrolytes can participate in forming the solid electrolyte interface (SEI) films³⁻⁷ and organic polymeric/gel-like layer⁷⁻⁹ via irreversible reduction decompositions in the negative potential range of 0–1.7 V (vs. Li⁺/Li) during the first cycle's Li ion intercalation (discharge) reactions, which can restrain the further decomposition of electrolytes as can be seen from the much smaller reduction current but the almost constant oxidation current of the second cycle (Fig. S2b). Based on the above reasons, the electrolytes can be stable in both positive and negative electrodes during the charge/discharge processes under 4.5 V capacitor's voltage.

Reaction mechanisms of the NiCo₂O₄ anode

The intercalation/de-intercalation reactions of Li ion inside the NiCo₂O₄ anode can be expressed as Eqs. (1)–(4).^{5–7,10} When NiCo₂O₄ are electrochemically discharged with Li-metal, the crystal structure destruction takes place followed by the formation of Ni and Co metal nanoparticles and Li₂O phase, as shown in Eq. (1). Then, during charge-reaction (Li-removal), both Ni and Co metal nanoparticles can reversibly react with Li₂O matrix by the displacement reaction forming the respective nanosize metal oxides (Eqs.(2) and (3)). In the most favorable case, the bivalent Co²⁺ (i.e., CoO) can further react with Li₂O to form bi/tri-valent Co₃O₄ as shown in Eq.(4). Therefore, during charge/discharge cycling, a total capacity corresponding to 7.33 recyclable moles of Li per mole of the starting material NiCo₂O₄ can be expected.



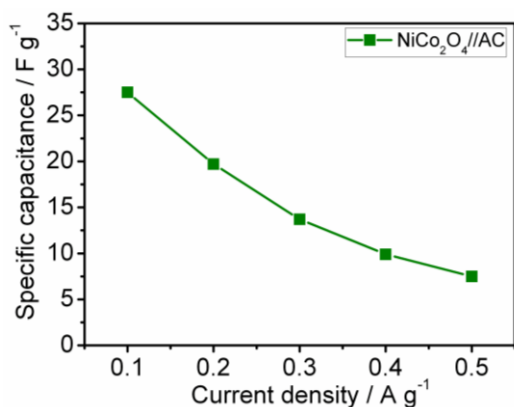


Fig. S3 Specific capacitance of hybrid NiCo₂O₄//AC Li ion capacitor as a function of current density.

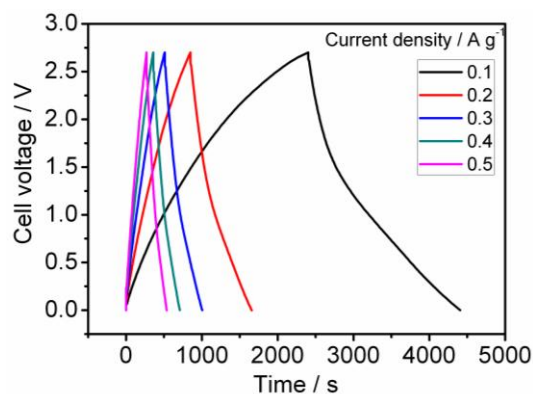


Fig. S4 CP curves of symmetric AC//AC Li ion capacitor.

Table S1 A comparison among different hybrid Li ion capacitors.

| Hybrid capacitors | Electrolytes | Capacitor voltage (V) | E_m -max (W h Kg ⁻¹) | P_m -max (W Kg ⁻¹) | Cycle life (loss) (current density) | Ref. |
|--|-------------------------------|-----------------------|------------------------------------|----------------------------------|--|-----------|
| CNF//LiCoPO ₄ | 1 M LiClO ₄ /EC:PC | 2.0 | 11 | 770 | 1000 (33 %) (0.5 mA cm ⁻²) | 11 |
| TiP ₂ O ₇ //AC | 1 M LiPF ₆ /EC:DMC | 3.0 | 13 | 371 | 500 (21.6 %) (31 mA g ⁻¹) | 12 |
| C-LiTi ₂ (PO ₄) ₃ //AC | 1 M LiPF ₆ /EC:DMC | 3.0 | 14 | 180 | 1000 (56 %) (30 mA g ⁻¹) | 13 |
| NiCo ₂ O ₄ //AC | 1 M LiPF ₆ /PC:DMC | 4.5 | 39.4 | 554 | 2000 (no loss) (300 mA g ⁻¹) | This work |

References

1. J. W. Xiao and S. H. Yang, *RSC Adv.*, 2011, **1**, 588.
2. T. Wu, J. Y. Li, L. R. Hou, C. Z. Yuan, L. Yang and X. G. Zhang, *Electrochim. Acta*, 2012, **81**, 172.
3. D. Aurbach and A. Zaban, *J. Electroanal. Chem.*, 1995, **393**, 43.
4. N. Munichandraiah, L. G. Scanlon and R. A. Marsh, *J. Power Sources*, 1998, **72**, 203.
5. R. Alcántara, M. Jaraba, P. Lavela, and J. L. Tirado, *Chem. Mater.*, 2002, **14**, 2847.
6. Y. N. Nuli, P. Zhang, Z. P. Guo, H. K. Liu and J. Yang, *Electrochem. Solid State Lett.*, 2008, **11**, A64.
7. Y. Sharma and M. Srinivasan, *AIP Conf. Proc.*, **1447**, 365.
8. S. Laruelle, S. Grugeon, P. Poizot,; M. Dolle, L. Dupont and J. M. Tarascon, *J. Electrochem. Soc.*, 2002, **149**, A627.
9. S. Grugeon, S. Laruelle, L. Dupont, J. M. Tarascon, *Solid State Sci.*, 2003, **5**, 895.
10. J. F. Li, S. L. Xiong, Y. R. Liu, Z. C. Ju and Y. T. Qian, *ACS Appl. Mater. Interfaces*, 2013, **5**, 981.
11. R. Vasanthi, D. Kalpana, N.G. Renganathan, *J. Solid State Electrochem.*, 2008, **12**, 961.
12. V. Aravindan, M. V. Reddy, S. Madhavi, S. G. Mhaisalkar, G. V. Subba Rao and B. V. R. Chowdari, *J. Power Sources*, 2011, **196**, 8850.
13. V. Aravindan, W. Chuiling, M. V. Reddy, G. V. Subba Rao, B. V. R. Chowdari and S. Madhavi, *Phys. Chem. Chem. Phys.*, 2012, **14**, 5808.