

Aqueous TiO₂/Ni(OH)₂ rechargeable battery with a high voltage based on proton and lithium insertion/extraction reactions

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Preparation of the α -Ni(OH)₂ and TiO₂ nanotube arrays.

α -Ni(OH)₂ was prepared by a homogeneous precipitation method as reported in our previous work.^[1] A mixed solution containing Ni(NO₃)₂•6H₂O, Al(NO₃)₃•9H₂O ($[Ni^{2+}] + [Al^{3+}] = 0.4$ M, $[Al^{3+}]/\{[Ni^{2+}] + [Al^{3+}]\} = 0.1$) and 2.0 M urea in a reaction container was constant agitated keeping in 90°C for 12 h. After aging in the mother solution for another 12 h at the same temperature, the green precipitates were separated by centrifugation, washed several times with de-ionized water to a neutral pH value, washed once with anhydrous ethanol, and dried at 60°C in air. TiO₂ nanotube arrays were prepared by anodizing of metallic titanium foils (0.25 mm thick, 99.7% purity, Sigma-Aldrich). Ti foil (2.3 cm×2.8 cm) coupled with the graphite counter electrode was subjected to the galvanostatic anodization under the current of 100 mA at 20°C for 52 min. The electrolyte was 0.4 wt% NH₄F and 1.76 wt% water in ethylene glycol. After anodization, the sample was calcined at 400°C in air for 30 min. The characterization of the sample was conducted by X-ray powder diffraction (XRD, RIGAKU D/Max-2500) and scanning electron microscopy (SEM, Hitachi 3500N).

Electrochemical measurement

The cathode was prepared by incorporating the paste composed of α -Ni(OH)₂, cobalt oxide powders, and Ni powders with a weight ratio of 65.6:7.7:26.7 with 1.0 wt% binder (hydroxypropyl methylcellulose, HPMC) into nickel foam, drying in 60°C and pressing into disk

under 30 MPa. The TiO₂ nanotube arrays on the titanium foil substrate were used directly as the anode. The cell was constructed with an excess of α -Ni(OH)₂ as the cathode, coupled with TiO₂ nanotube arrays as the anode, and a mixed aqueous solution of 1.5 M LiOH and 4 M KOH as the electrolyte. Cyclic voltammetry was performed in a three-electrode electrochemical cell with mixed 1.5M LiOH + 4.0M KOH electrolyte. In the case of TiO₂ nanotube arrays, the Ni(OH)₂ and Hg/HgO were used as the counter and reference electrodes, respectively. As for the Ni(OH)₂, a nickel foam and Hg/HgO were used as the counter and reference electrodes, respectively. Galvanostatic charge and discharge tests were performed with a two-electrode cell at a charge current rate of 3.54 mA/cm² (ca. 4.0 C, 1 C=168 mA/g) and the discharge rate of 1.77 mA/cm² (ca. 2.0 C), which are based on TiO₂ nanotube arrays as the active materials. The discharge cut-off voltage of the cell was 1.0 V. The different mass of the Ti electrode before and after peeling off the TiO₂ film was used to calculate the discharge capacity. All the electrochemical tests were performed at ambient temperature.

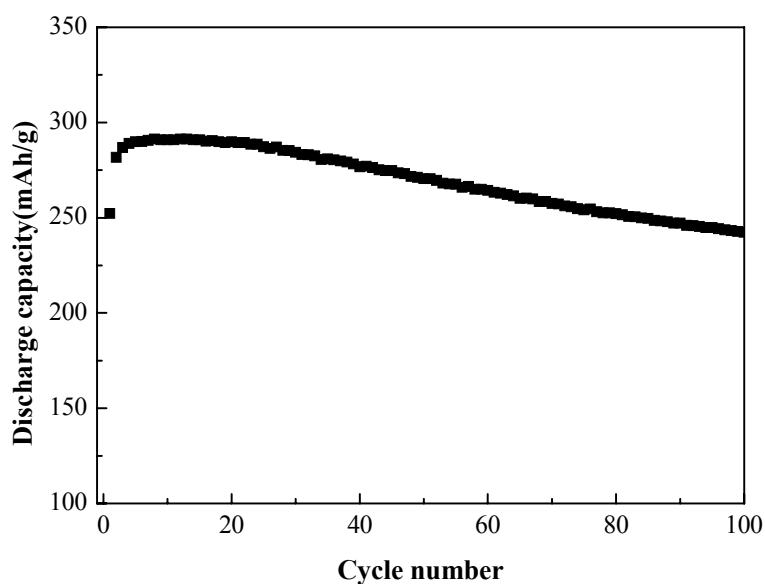


Figure S1. Cycle performance of the α -Ni(OH)₂ electrode in a mixed electrolyte of 1.5M LiOH and 4M KOH.

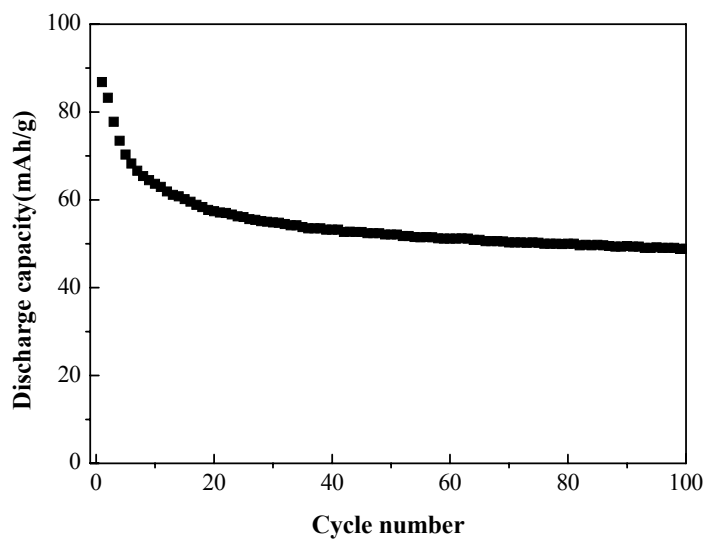


Figure S2. Cycle performance of the TiO₂ nanotube arrays in 1.5M LiOH aqueous electrolyte.

References

- (1) 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.