Supporting Information

Interlayer expansion of hydrogen titanate anodes improves electrochemical Na^+ intercalation kinetics and reversibility

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Materials and Methods

Hydrogen tetratitanate ($H_2Ti_4O_9$, referred to as HTO) was synthesized through a solid-state synthesis method. Initially, potassium tetratitanate ($K_2Ti_4O_9$) was obtained by heating a mixture of potassium carbonates (K_2CO_3, VWR Chemicals) and titanium (IV) oxide (TiO_2, Thermo Scientific) in a 1:3.5 molar ratio at 800 °C for 20 h in a muffle furnace (Nabertherm P330) and followed by an additional 20 h after grinding with a mortar and pestle. To obtain HTO, 1 g of $K_2Ti_4O_9$ was stirred in 200 mL of 1 M hydrochloric acid (HCl, VWR Chemicals) for 3 days at 60 °C, with the acid solution being changed daily to remove the exchanged K^+. The resulting product was then filtered and dried at room temperature under air flow before further characterization.

Propylamine-pillared HTO, HTO-PA, was synthesized by stirring 200 mg of HTO powder in 6.66 ml of a 50 vol.% aqueous solution of propylamine (C_3H_9N, Thermo Scientific) for 72 hours at room temperature. HTO-PA powder was recovered by vacuum filtration, then washed several times with deionized water until neutral pH was reached. The obtained HTO-PA powder was left to dry in circulating air at room temperature.

Powder X-ray diffraction (XRD) patterns of the samples were obtained using a Bruker D8 Advance equipped with a Cu Kα radiation source ($\lambda = 0.15406$ nm). The patterns were recorded in Bragg-Brentano mode in the 2θ range between 2° and 40° with 0.02° step size.

Atomic force microscopy (AFM) measurements were recorded using a Bruker Dimension Icon and a SCM-PIT-V2 tip (Bruker, nominal spring constant 3 N/m) in tapping mode. The powder sample was dispersed in *N*-Methyl-2-pyrrolidone (NMP) solution, then drop cast on a glassy carbon substrate and left to dry in circulating air overnight.

Scanning electron microscopy (SEM) imaging was performed using a ZEISS Crossbeam 340 electron microscope operated at 5 kV and working distance of 7.4 mm.

The synthesized powders were used to make electrode slurries where the active material, conductive carbon (C-NERGY Super C65), and polyvinylidene fluoride (PVdF, Solvay) binder (2 wt.% PVDF dispersed in *N*-Methyl-2-pyrrolidone, NMP, Thermo Scientific) were mixed in a 8:1:1 mass ratio. The slurry was then cast onto carbon-coated Al current collectors (20 µm, battery grade, Welcos) using a doctor blade with a wet film thickness set to 60 µm, resulting in mass loading of ca. 0.6-0.7 mg/cm^2. The low mass loading is favorable to avoid kinetic limitations caused by electrode architecture, allowing to focus the study on fundamental materials properties. The cast slurries were set to dry overnight in circulating air, then subsequently cut into 12-mm discs and dried overnight in vacuum at room temperature.

Except for dilatometry, all electrochemical measurements were performed in coin cells (type CR2032) in a 2-electrode configuration against 12 mm diameter Na disc electrodes (Acros Organics, 99.8%). 150 µL of 1M $NaPF_6$ (battery grade, FluoroChem) in 1:1 vol% EC:PC (battery grade, UBE) was used as electrolyte, and a 19 mm diameter Whatman glass microfiber (grade GF/A) was used as a separator. The measurements were conducted in temperature-controlled climatic chambers set at 20 °C.

Galvanostatic intermittent titration technique (GITT) measurements were conducted in coin cells after one galvanostatic cycle at 50 mA g^{-1} current rate. The measurements were performed by applying a 30-minute, 20 mA g^{-1} current pulse followed by a 2-hour rest. The apparent ion diffusion coefficient (D) was estimated using the equation[1]:

$$D = \frac{4}{\pi\,\tau}\left(\frac{m_B\,V}{M_B\,A}\right)^2\left(\frac{\Delta E_s}{\Delta E_t}\right)^2$$

where τ is the current pulse duration, m_B is the active material mass, V is the molar volume, M_B is the molar mass, A is the geometrical electrode area[2], and ΔE_s and ΔE_t are the change of steady voltage and the total transient cell voltage change, respectively.

Electrochemical dilatometry (ECD) measurements were conducted using an ECD-4-nano dilatometer (EL-CELL). Free-standing electrodes were prepared by mixing the active material, conductive carbon (C-NERGY Super C65), and polytetrafluoroethylene (PTFE, 60 wt.% aqueous solution, Sigma-Aldrich) in a mass ratio of 8:1:1. Once the mixture achieved a dough-like consistency, it was calendared to form a sheet with a uniform thickness of ca. 40–60 µm. The sheet was then dried under vacuum at 60 °C, and 8 mm electrodes were subsequently punched out.

The assembly of the cell was conducted in an argon-filled glovebox (M-Braun), with H_2O and O_2 content below 1 ppm. In a first step, a round metallic sodium disc (10 mm), serving as the counter electrode, was placed on a metal plate supported by a spring. A Whatman glass microfiber separator (Grade GF/A) with a 10 mm diameter was placed on top of the sodium counter electrode and soaked with 50 µL of electrolyte. Above the separator, a sintered glass component in the shape of a T-frit was positioned to act as both an electrolyte reservoir and a separator between the counter and working electrodes. The T-frit was pre-soaked with 500 µL of electrolyte before assembly. The counter electrode, separator, and T-frit were secured in a polyetheretherketone (PEEK) unit, which was immobilized onto an ECD platform using a hex screw to prevent movement of the counter electrode base. Following this, the working electrode (HTO or HTO-PA) with a diameter of 8 mm was placed at the center on top of the sintered glass T-frit. The top screw-cap unit was then tightened with thrust screw. After assembly, the ECD cell was allowed to rest at open circuit potential (OCP) for 6 hours before the electrochemical measurements. All ECD measurements were carried out in a climate-controlled chamber (Binder) at 22 °C.

References

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