Nano-Silicon/Reduced Graphene Oxide Composite Anodes for High Performance All Solid-State Batteries

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Experimental methods

Preparation of reduced graphene oxide (rGO) powder: First, Graphite oxide (GO) was produced from natural graphite (SP-1, Bay Carbon, Inc.) by using modified Hummers method. The prepared GO flakes (0.4 g) were dispersed in distilled water (40 mL) using ultrasonication for 100 min to produce homogeneous aqueous colloidal suspensions. The resulting GO suspensions were transferred into a Teflon-lined autoclave with 100 mL capacity and hydrothermally treated at 180 °C for 6 h. The product was filtered and washed five times with distilled water, with a final wash using ethyl alcohol. The filtered rGO product was dried under oven at 80 °C overnight.

Preparation of n-Si/G powder: The GO flakes (0.3 g) and Si nano powder (n-Si) (0.6 g, > 98%, 30-50 nm, Nanostructured & Amorphous Materials, Inc.) were dispersed in distilled water (40 mL) and in ethyl alcohol (20 mL), respectively. Each dispersion was ultrasonicated for 100 min, followed by mixing in a volumetric flask and stirring at 75 °C overnight. The mixture was transferred into a Teflon-lined autoclave and hydrothermally with 100 mL capacity and hydrothermally treated at 180 °C for 6 h. The resulting hydrogel was filtered and washed using

ethyl alcohol. The filtrate (hereafter referred to as n-Si/G) was ground and dried at 80 ℃ overnight.

Sample characterizations: Prepared powder samples were analyzed using field-emission scanning electron microscopy (SEM, Apero, Thermo Scientific, USA), transmission electron microscopy (TEM, Titan G2, FEI, USA), scanning transmission electron microscopy (STEM, Themis Z, Thermo Scientific, USA) with energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS, Nexsa G2, Thermo Scientific, UK). Cross-sectional analysis of cycle-aged n-Si and n-Si/G anodes was performed using focused ion beam (FIB) – SEM (Helios NanoLab 600, FEI, USA).

Preparation of electrodes and solid-state battery (SSB) cells: The anode active material, polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS, Sigma Aldrich) binder, and Li_6PS_5Cl (MSE Supplies) solid electrolyte (SE) powders were mixed in a ratio of 60:1:40 with butyl butyrate (Sigma Aldrich) solvent to form a slurry. The prepared slurry was casted onto a Cu foil using a 120 µm doctor blade followed by drying overnight inside Ar-filled glove box. SSB full cells were assembled by first pelletizing 100 mg of in-house prepared $Li_6PS_5Cl_{0.5}Br_{0.5}$ solid electrolyte under a pressure of 150 MPa. Subsequently, $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ cathode (coated with 1 wt% $LiNbO_3$) and either an n-Si or n-Si/G anode were pressed onto opposite sides of the pellet at 700 MPa. Electrochemical performance of the assembled SSB cells was evaluated under a constant stack pressure of 5 MPa. All the cells were tested using battery testing stations (Arbin LBT) at room temperature (RT). Electrochemical impedance spectroscopy was measured on full-cells at 50% state of charge (SOC) using a potentiostat (Gamry Reference 600+) in a frequency range of 5 MHz - 50 mHz. The resulting Nyquist plots were further processed via distribution of relaxation time (DRT) technique using MATLAB code developed by Wan et al.[1]

Reference

1 T.H. Wan, M. Saccoccio, C. Chen, F. Ciucci, *Electrochim. Acta*, 2015, **184**, 483–499.