

Supplementary information

Ultra-small nanoparticles of MgTi₂O₅ embedded in carbon rods with superior electrochemical performance for sodium storage

Fangxi Xie,^a Yuanfu Deng,^{*b,c} Ye Xie,^b Hongjie Xu^d and Guohua Chen^{*a,c,d}

^a Centre for Green Products and Processing Technologies, Fok Ying Tung Graduate School, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, P. R. China;

^b The Key Laboratory of Fuel Cell Technology of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, China, chyfdeng@scut.edu.cn;

^c Centre for Green Products and Processing Technologies, Guangzhou HKUST Fok Ying Tung Research Institute, Guangzhou, 511458, China;

^d Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, P. R. China, kechengh@ust.hk

Experimental

Material preparations: All chemical reagents are in A.R. grade and used as received. The MgTi₂O₅/C composite material was synthesized according to the modified method previously reported.^[29] First of all, 6.30 g of citric acid, 3.40 ml of titanium butoxide and 0.20 g magnesium oxide was added in order in 50 ml of distilled water. The pH was tuned to 2.0 with ammonia. The solution was heated to 60 °C to accelerate the reaction and dissolve the complex. 5.0 g of Polyvinylpyrrolidone (PVP) is added into this clear solution to modify the morphology of final product. After some solvent is vaped, the solution is allowed to cool down to room temperature. The white precipitates were collected through filtration and washed with ethanol and dried in vacuum at 60 °C. The precursor was sintered in a tubular furnace at 600 °C for 2 h under Ar atmosphere to obtain the final product, which is named as MTO-Ar. The precursor sintered in a tubular furnace at 600 °C for 2 h under air atmosphere would be named as MTO-Air.

And both of the post-calcination samples were calcined at 450 °C under Ar with 5 % O₂, which was employed to prevent the fast consumption of carbon and the induced aggregation of MgTi₂O₅ nanoparticles. And these two samples named as MTO-Ar-PC-2h and MTO-Ar-PC-12h according to their post-calcination time, respectively. And the carbon was synthesized through pyrolysis process of (NH₄)₃Hcit at 600 °C for 2 h under Ar atmosphere.

Material Characterization: The products were characterized by powder X-ray diffraction (XRD, Bruker D8), scanning electron microscope (SEM, JEOL 6700F), transmission electron microscope and element mapping (TEM, JEOL 2010 200kV) and high-resolution transmission electron microscope (HRTEM, JEOL 2010F 200kV). Raman spectrum was obtained with a Bio-Rad FTS6000 Raman spectroscopy with a 532 nm blue laser beam. Thermogravimetric (TG) analysis was carried out using a Netzsch STA 409EP thermal analyzer with a heating rate of 10 °C min⁻¹ in air.

Electrochemical investigation: The as-synthesized material was mixed with acetylene black and polyvinylidene fluoride (PVDF) (70:20:10, w/w/w) in *N*-methyl-2-pyrrolidone (NMP). Then the slurry was spread on copper foil and dried at 80 °C overnight in a vacuum oven. The CR2025 type coin cell battery testing were assembled in an argon-filled glove box (MB20G, MBraun) with the pure sodium metal as the counter electrode, glass fiber membrane (Whatman GF/C, England) as the separator and the 1M NaClO₄ (ethylene carbonate: propylene carbonate =1:1,v/v) as the electrolyte. The cells were electrochemically cycled between 0.01 and 2.7 V at different charge/discharge rates on a multichannel battery test system (LANHE, Model CT2001C). The specific capacity was calculated based on the total mass of MgTi₂O₅/C composite. The cyclic voltammetric (CV) tests were carried out on a Versa-stat 3 electrochemical workstation (Princeton Applied Research) at a scan rate of 0.1 mV/s. The electrochemical impedance spectroscopy (EIS) data of the electrodes were acquired at room temperature, using a ZENNIUM electrochemical workstation (ZAHNER-Elektrik GmbH & Co.KG) after a desired number of cycles in

the frequency range from 100 kHz to 10 mHz by imposing an alternate current with an amplitude of 10 mV on the electrode.

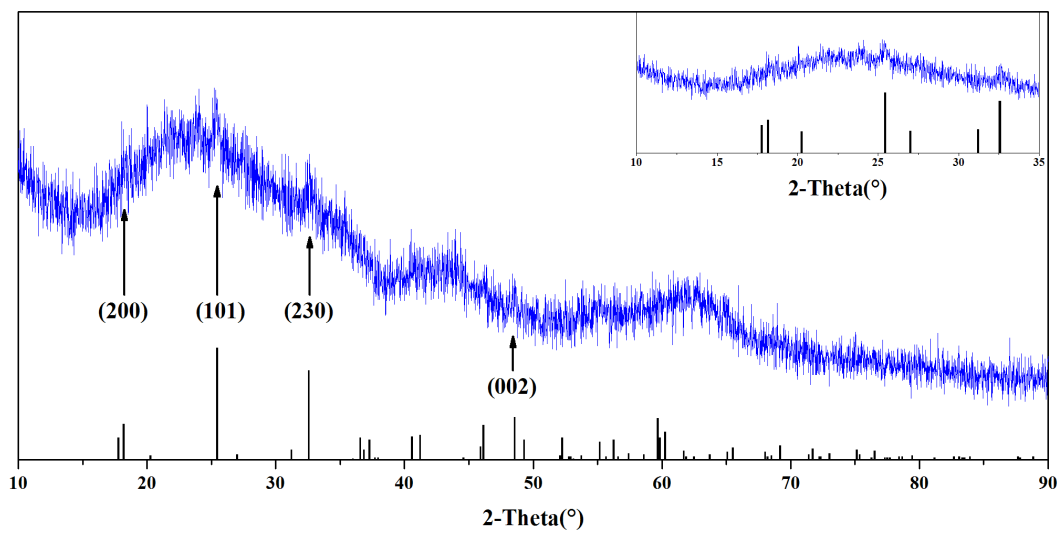


Figure S1 The detailed XRD patterns of MTO-Ar.

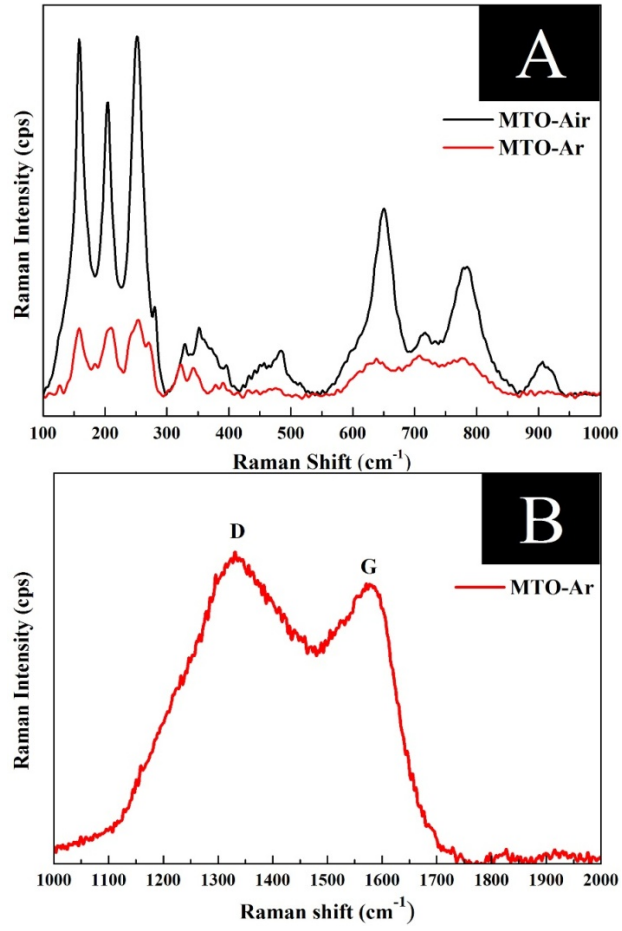


Figure S2. The Raman Spectra of MTO-Ar and MTO-Air.

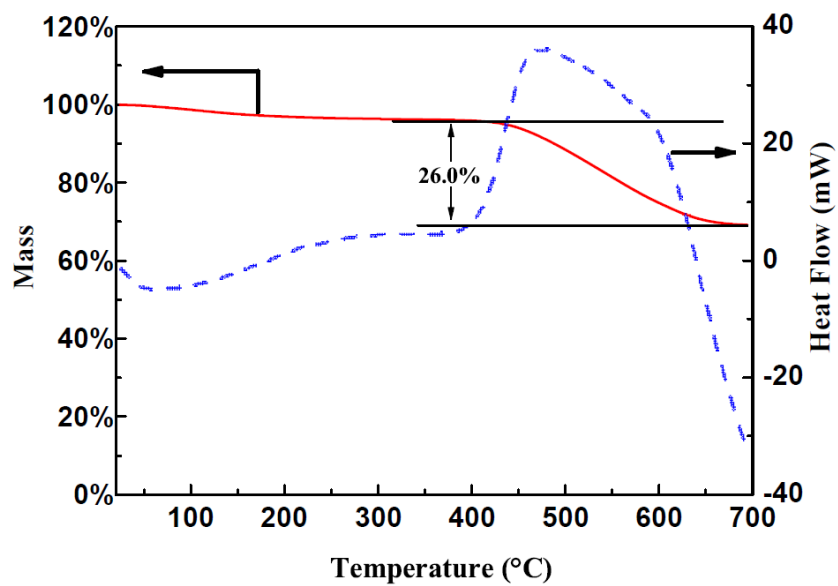


Figure S3. Thermogravimetric analysis of MTO-Ar in air at the heating rate of 10 °C/min.

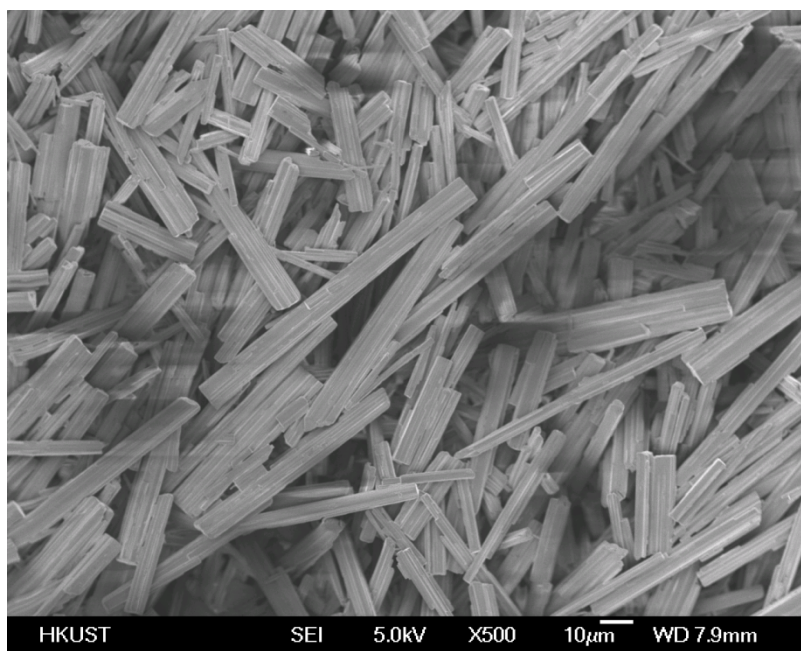


Figure S4. The scanning electron microscope image of precursor $(\text{NH}_4)_2\text{Mg}(\text{H}_2\text{O})_6[\text{Ti}(\text{C}_6\text{H}_6\text{O}_7)_3]_2 \cdot 6\text{H}_2\text{O}$.

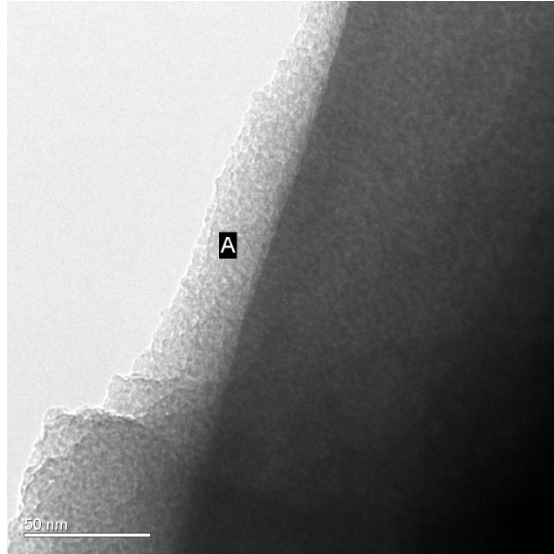


Figure S5. The spots of element mapping of transmission electron microscope image of MTO-Ar.

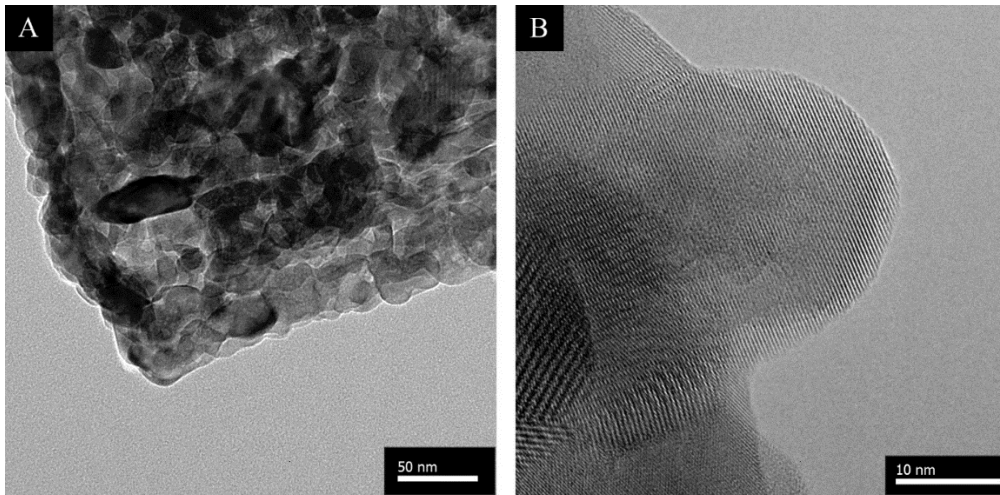


Figure S6. (A) The low magnification transmission electron microscope image of MTO-Air; and (B) The high magnification transmission electron microscope image of MTO-Air.

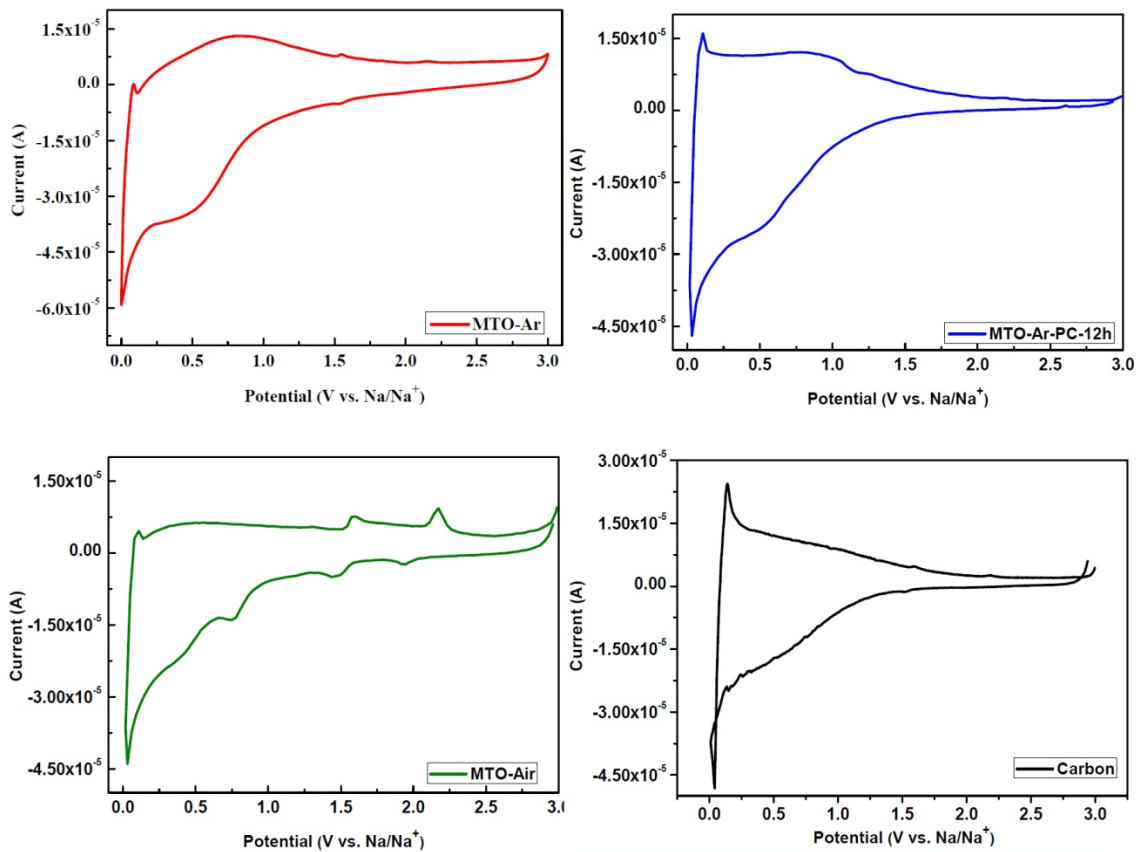


Figure S7. The CVs in the third cycle for the MTO samples with different carbon content in sodium ion batteries.

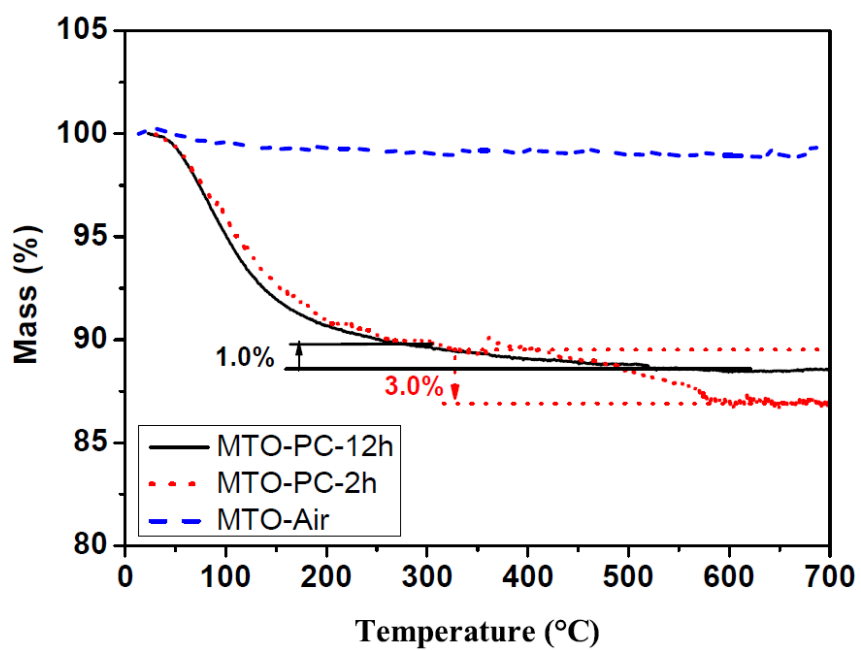


Figure S8 The Comparison of TGA curves of MTO-Ar-PC-2h, MTO-Ar-PC-12h and MTO-Air in air at the heating rate of 10 °C/min.

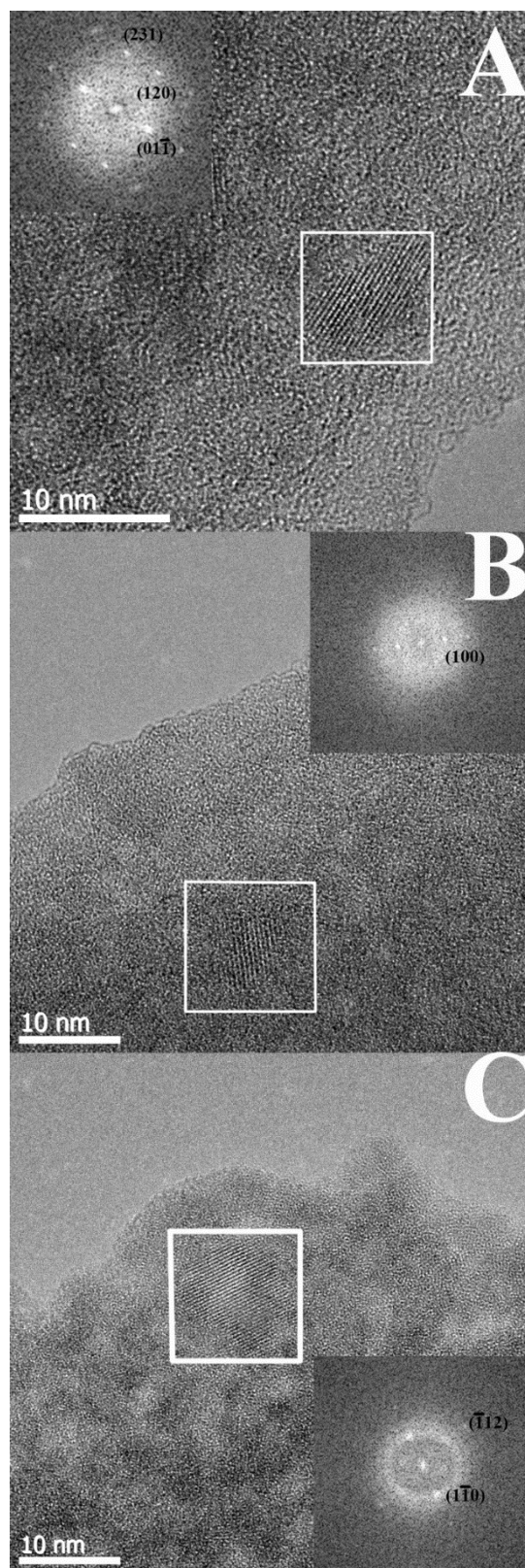


Figure S9. The HRTEM and FFT images to selected area of (A) MTO-Ar, (B) MTO-Ar-PC-2h and (C) MTO-Ar-PC-12h.

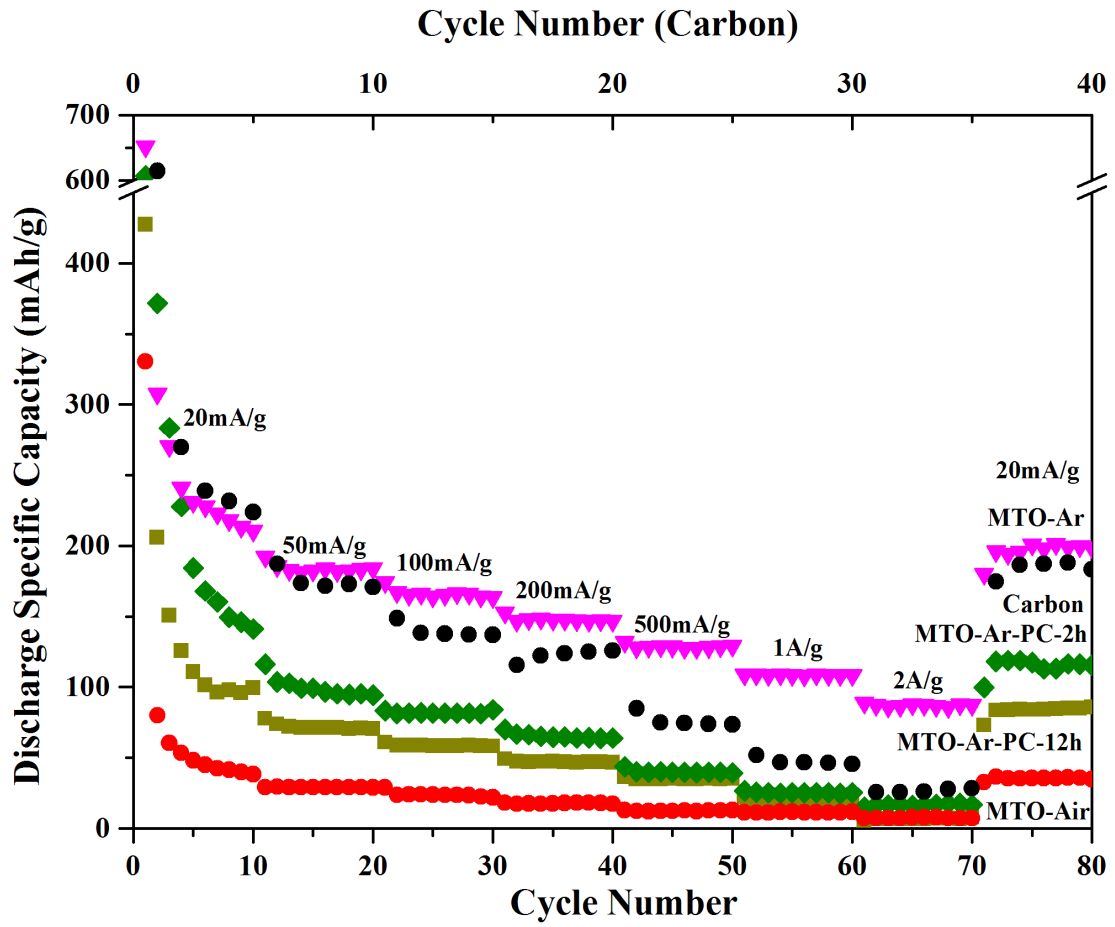


Figure S10. The comparison of specific capacities of MTO-Ar, carbon, MTO-Ar-PC-2h, MTO-Ar-PC-12h and MTO-Air under different current densities for SIBs.

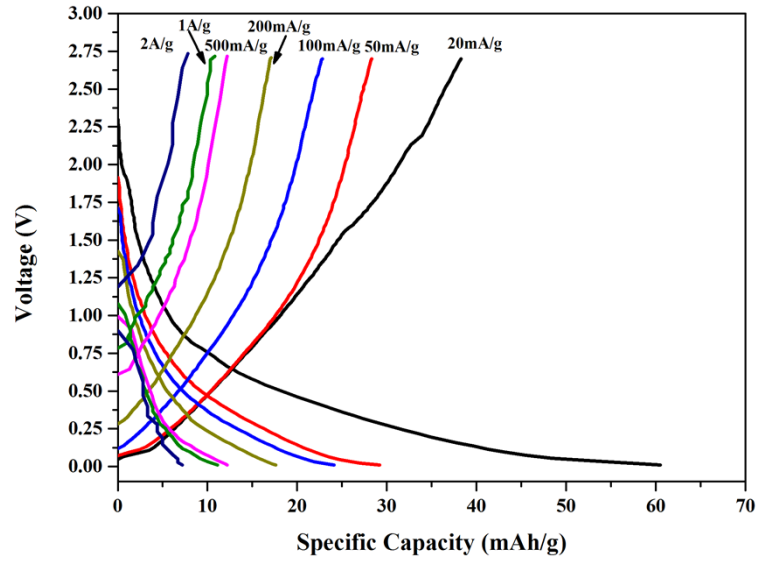


Figure S11. The discharge-charge profiles of MTO-Air under different current densities.