Electronic Supplementary Information

Ultrahigh rate capability and long cycling stability of dual-ion batteries enabled by TiO₂ microspheres with abundant oxygen vacancies

Tong Mu,^{ab} Jiguang Zhang,^{*ab} Rui Shi,^{ab} Yunfeng Zhu,^{*ab} Jinglian Zhu,^{ab} Yana

Liu,^{ab} Yao Zhang^c and Liquan Li^{ab}

^a College of Materials Science and Engineering, Nanjing Tech University, 30 South Puzhu Road, Nanjing 211816, P. R. China.

^b Jiangsu Collaborative Innovation Centre for Advanced Inorganic Function Composites, Nanjing Tech University, Nanjing 211816, PR. China

^c School of Materials Science and Engineering, Southeast University, Nanjing 211189, PR. China

Experimental Section

Synthesis of TiO_{2-x} and TiO₂

The synthesis routine of TiO_{2-x} included the preparation of precursor H₂TiO₃ and the sequent calcination of the mixture with H₂TiO₃ and urea. H₂TiO₃ was prepared according to literature reported with some modification.¹ In a procedure of H₂TiO₃, a mixture of (NH₄)₂TiF₆ (0.6 g) and urea (1.2 g) was added to a mixed solution of 7.5 ml H₂O₂ and 30 ml H₂O under magnetic stirring 0.5 h to obtain the dark brown solution. Then the solution was transferred to a 50 ml Teflon-lined autoclave and heated at 200°C for 10h. The resulting white cooling product was collected through washing with deionized water three times. Afterwards, the washed product was dispersed in 25 ml of NaOH solution (10 M), followed by hydrothermal reaction at 140°C for 2 h in a 50 ml Teflon-lined autoclave. Then, the precipitate Na₂TiO₃ was collected, ion exchanged via 300 ml of HCl aqueous solution (0.1 M) under magnetic stirring, washed with deionized water and dried under vacuum at 60 °C for 12 h to obtain precursor power hydrogen titanate (H₂TiO₃). To obtain TiO_{2-x}, the precursor H₂TiO₃ (1.0 g) was mixed with urea (3.0 g), which was further annealed at 550°C for 2 h under air with the ramping rate of 10 °C min⁻¹ in a Muffle furnace. In contrast, TiO₂ without oxygen defects was also fabricated by direct calcination of 1.0 g of H₂TiO₃ power under the same conditions without urea.

Preparation of Electrolyte

The electrolyte was carried out in argon-filled glove box according to literature reported before.² First, 0.6667 g of anhydrous aluminum chloride power (AlCl₃) was dissolved in 7.5 ml THF slowly and stirred 12 h to obtain solution A. Then 5 ml phenyl was added in solution A slowly and stirred 12 h to get solution B. To obtain dual Mg/Li-ion battery electrolyte, 0.2112 g LiCl was added into the configured solution B and stirred 12h.

Electrochemical and Material Characterizations

The working electrodes were fabricated by mixing the as-prepared samples, acetylene black (AB) and polyvinylidene fluoride (PVDF) in N-methyl-pyrrolidinone (NMP) solvent at a weight ratio of 8:1:1. The mixture was stirred for 4 h, coated on graphite foil, and dried at 100 °C in a vacuum oven. The loading mass of active materials is about 1.1-1.5 mg cm⁻². The electrochemical performance was tested via CR2032 coin cells, assembled by magnesium foil as both counter and reference electrode, glass fiber film (Whatman, GF/F) as the separator, 0.4 M APC+ 0.4 M LiCl as the electrolyte, and as-prepared samples as the working electrodes. The

galvanostatic discharge/charge tests were carried out on a Neware battery test system in a voltage range of 0.01-2.0 V (vs. Mg^{2+}/Mg) at different current densities under ambient temperature. The cyclic voltammetry was collected using a CHI600E electrochemical workstation.

Sample characterization

Powder X-ray diffraction (XRD) was carried out utilizing an X-ray diffractometer (Bruker D8 diffractometer) using Cu K α (λ =1.5406 Å) radiation with a scan rate of 5 °C/min. Scanning electron microscopy (SEM) was tested by JEOL JSM-7600F equipped with energy dispersive X-ray spectroscopy (EDS) to characterize the microstructure of the samples. Electron paramagnetic resonance (EPR) measurement was conducted on a Bruker A300 spectrometer. X-ray photoelectron spectrometer (XPS) was collected on a Kratos AXIS ULTRA DLD system. The electronic conductivity of the as-prepared samples was conducted on a four-point probe equipment (ST-2722, Jingge).

Computational Method.

A supercell of $2 \times 2 \times 2$ was constructed for the DFT calculations. The TiO_{2-x} with different oxygen vacancy rate was moduled by removing the different amount of oxygen atoms from the s upercell. The final chemical formula of 3 modules were Ti₃₂O₆₄, Ti₃₂O₆₃ and Ti₃₂O₆₂, respectively. The calculations were performed with Vienna Ab-initio Simulation Package (VASP) code based on density functional theory.^{3,4} The projector augmented wave (PAW) was adopted to simulate the wave function of the electrons and the cutoff energy the PAW was set to 400 eV.⁵ The Perdew-Burke-Emzerhof (PBE) realization of generalized gradient approximation (GGA) was used to describe the exchange-correlation potential of the electrons.^{6,7} A 4 \times 4 \times 2 k-point mesh with Gamma centred was used for geometry optimization, and a denser mesh of 7 \times 7 \times 3 mesh was used for the calculations of the density of states.⁸ The force on the atoms was less than 2 \times 10⁻² eV/Å during the geometry optimization.



Fig. S1 SEM image of the contrast sample TiO₂.



Fig. S2 SEM image of TiO_{2-x}.



Fig. S3 SEM image of TiO_{2-x} at higher magnification and its corresponding

elemental mapping.



Fig. S4 CV curves at different scanning rates of Mg|APC + LiCl|TiO_{2-x} cell.

Table S1. Summary of electrochemical performance of the current state-of-the-art
materials as cathode materials for dual Mg/Li-ion batteries.

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Samples	Electrolyte	Rate capability	Cycling stability	Ref.		
Commerical TiO ₂	$0.4 \text{ M} \text{Mg}(\text{BH}_4)_2 +$	85 mAh g^{-1} at	~130mAh g ⁻¹ at 27.2 mA $\sigma^{-1}(00 \text{ guales})$	9		
	0.4 WI LIDH4/10	270 mA g ⁻¹	g (90 cycles)			
1D mesporous	0.5 M Mg(BH ₄) ₂ +	130 mAh g ⁻¹	~115mAh g ⁻¹ at 672 mA g ⁻¹	10		
TiO ₂	1.5 M LiBH ₄ /TG	at 336 mA g^{-1}	(6000 cycles)			
TiO ₂ -B nanowires	0.4 M APC + 0.4	125mAh g ⁻¹ at	$\sim 205 \text{ mAh g}^{-1} \text{ at } 200 \text{ mA}$	11		
	M LiCl/THF	1000 mA g^{-1}	g ⁻¹ (200 cycles)			
VTi _{2.6} O _{7.2}	0.25 M APC + 1 M	$65 \text{ mAh g}^{-1} \text{ at}$	~98 mAh g ⁻¹ at 1000 mA	12		
nanocrystals	LiCl/THF	2000 mA g ⁻¹	g ⁻¹ (1200 cycles)			

Ti0.78[]0.22O1.12F0.40	0.2 M APC + 1 M	195 mAh g ⁻¹ at	~175 mAh g ⁻¹ at 1000 mA	13
(OH) _{0.48}	LiCl/THF	1000 mA g ⁻¹	g ⁻¹ (400 cycles)	
Prelithiated V ₂ C	0.4 M APC + 0.4	82.3 mAh g^{-1} at	~106 mAh g ⁻¹ at 50 mA g ⁻¹	14
MXene	M LiCl/THF	500 mA g^{-1}	(480 cycles)	
TiS ₂	0.4 M APC + 0.4	$65 \text{ mAh g}^{-1} \text{ at}$	~ 119 mAh g ⁻¹ at 80 mA g ⁻¹	15
	M LiCl/THF	480 mA g^{-1}	(400 cycles)	
V ₂ MoO ₈	0.4 M APC + 1 M	98 mAh g^{-1} at	~ 132 mAh g ⁻¹ at 20 mA g ⁻¹	16
	LiCl/THF	500 mA g^{-1}	(50 cycles)	
Li ₄ Ti ₅ O ₁₂	0.25 M APC +	110 mAh g^{-1} at	~ 175 mAh g ⁻¹ at 15 mA g ⁻¹	17
	0.25 M LiCl/THF	300 mA g^{-1}	100 cycles)	
MoS ₂ /graphere	0.25 M APC +	186 mAh g^{-1} at	~ 170 mAh g ⁻¹ at 500 mA	18
	0.25 M LiCl/THF	500 mA g^{-1}	g ⁻¹ (500 cycles)	
VO ₂	0.25 M APC + 1 M	138.3 mAh g ⁻¹ at	~ 156 mAh g ⁻¹ at 20 mA g ⁻¹	19
	LiCl/THF	500 mA g^{-1}	(100 cycles)	
Mo ₆ S ₈	0.4 M APC + 1 M	$104.5 \text{ mAh g}^{-1} \text{ at}$	$\sim 100 \text{ mAh g}^{-1} \text{ at } 1932 \text{ mA}$	20
	LiCl/THF	1932 mA g^{-1}	g ⁻¹ (3000 cycles)	
MoO ₂ hollow	0.4 M APC + 0.4	150 mAh g^{-1} at	$\sim 162 \text{ mAh g}^{-1} \text{ at } 20 \text{ mA g}^{-1}$	21
microspheres	M LiCl/THF	100 mA g ⁻¹	(50 cycles)	
(NiCoMn) ₃ O ₄	0.4 M APC + 1 M	96 mAh g ⁻¹ at	~ 277 mAh g ⁻¹ at 100 mA	22
hollow spheres	LiCl/THF	2500 mA g^{-1}	g^{-1} (100 cycles)	
TiO _{2-x}	0.4 M APC + 0.4	110 mAh g^{-1} at	\sim 91mAh g ⁻¹ at 1680 mA g ⁻¹	This
microspheres	M LiCl/THF	1680 mA g ⁻¹	(2500 cycles)	work
		80 mAh g^{-1} at		
		3360 mA g^{-1}		

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