Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2017

Nanofiber networks of Na₃V₂(PO₄)₃ as cathode materials for high

performance all-solid-state sodium-ion batteries

Rongtan Gao,[†] Rui Tan,[†] Lei Han, Yan Zhao, Zijian Wang, Luyi Yang^{*} and Feng Pan^{*} School of Advanced Materials, Peking University, Peking University Shenzhen Graduate School, Shenzhen 518055, China. Tel: 86-755-26033200; E-mail: panfeng@pkusz.edu.cn. Synthesis of the NVP-F and NVP-S: First, 0.182 g vanadium pentoxide (V_2O_5) and 60 mL N, N-dimethyl formamide (DMF) were added into a round-bottom flask and stirred at 80 °C for 0.5 h, followed by the addition of 0.360 g sodium dihydrogen phosphate (NaH₂PO₄), 0.378 g oxalate dehydrate (H₂C₂O₄·2H₂O) and 10 mL deionized water (DI). The above solution was stirred for another 0.5 h and then transferred into a 100 mL autoclave followed by heated at 180 °C for 30 h. 0.180 g glucose was added into the Teflon-container and stirred for 0.5 h. The NVP-F precursor was obtained by keeping the above solution in an air oven at 70 °C overnight. Finally, the precursor was heated at 400 °C for 4 h and 700 °C for 8 h in Ar atmosphere at the heating rate of 3 °C min⁻¹ to get the Na₃V₂(PO₄)₃-F. For comparison, NVP-sphere (NVP-S) precursor was obtained by shorten the solvothermal process to 15 h followed by sintered at 700 °C in Ar atmosphere at a faster heating rate of 10 °C min⁻¹ without a preheating process.

Preparation of the PEO-Al₂O₃-NaClO₄ electrolyte membrane: Polyethylene oxide (PEO, $M_w=4\times10^6$) and sodium perchlorate (NaClO₄) were dissolved in acetonitrile (CH₃CN), with a molar ratio of ethylene oxide unit and lithium of 15 : 1 (5 : 1, 10 : 1, 20 : 1). Then 5 wt% (1 wt%, 2 wt%, 8 wt%, 10 wt%, 15 wt%), of nano-size aluminium oxide (Al₂O₃, Sigma-aldrich, the size is 30~50 nm) was added into the above solution. Then the mixture was stirred for 24 h to form a homogenous colloid. After that, cast the above mixture onto a Teflon substrate and heat it at 80 °C for 24 h to let the solvent evaporate and form the PEO-Al₂O₃-NaClO₄ electrolyte membrane. The obtained membranes are white and homogeneous and their thickness are all approximately 40 μ m.

Preparation of the coin-type half cells: NVP-F and NVP-S are mixed with acetylene black and poly(vinylidene fluoride) (PVDF) in a weight ratio of (5:3:2) in NMP, respectively. Then cast the above mixture onto aluminum foil and dry it at 80 °C in a vacuum oven to obtain the cathode plate. The loading of active materials (NVP) in every cathode plate ranges from 0.7 mg cm⁻² to 1.0 mg cm⁻². Then, the components' ratio was adjust to 7:2:1, in order to get the thicker cathodes, of which the loading of active materials ranges from 2.2 mg cm⁻² to 2.7 mg cm⁻². Finally, the cathode plate, electrolyte membrane and Na plate were stacked up in a 2032 coin cell to assemble the all-solid-state battery. For comparison, electrolyte membrane was replaced by 35 µL liquid electrolyte (1 M NaClO₄ in EC : DMC = 1 : 1) in order to assemble common liquid-state batteries.

Materials characterization: The morphological characterizations were observed by a scanning electron microscope (SEM, ZEISS Supra 55) and transmission electron microscopy (TEM, JEM-3200FS, 300kV). The X-ray diffraction (XRD) patterns of $Na_3V_2(PO_4)_3$ were collected from a Bruker D8 Advance diffractometer using Cu-K α radiation at room temperature, from 10° to 60° (The scan speed is 1.15° min⁻¹). The thermal properties were studied by thermogravimetric analysis (TG) carried out on a TGA/DSC1 system and DSC (DSC1). The specific surface areas of the cathode materials were measured by recording nitrogen adsorption and desorption isotherms on a Micromeritics surface area and porosity analyzer (ASAP 2020 HD88) and the data were analyzed with the Brunauer-Emmett-Teller (BET) theory.

Electrochemical measurements: The decomposition voltages were studied by electrochemical workstation (CHI 660E) between open-circuit voltage and 7.0 V at a scan rate of 0.5 mV/s. The cyclic voltammetry (CV) results were conducted by electrochemical workstation (CHI 660E) between 2.3 and 3.9 V at a scan rate of 0.5 mV/s. The EIS spectra were obtained from 10 kHz to 0.1 Hz. Ionic conductivity and Electrochemical Impedance were studied by electrochemical workstation (CHI 660E). The ionic conductivity of different electrolytes can be obtained by the equation (S1)

$$\sigma = L / (R * S) \tag{S1}$$

where L is the thickness of the electrolyte films, R is the resistance tested by EIS and S is the area of the electrolyte films. The galvanostatic charge-discharge experiments (e.g. rate tests, long-term cycling tests, etc) were performed on a Land instrument (Wuhan Land electronic Co., Ltd. China) with tests using cut-off voltages of 2.3 V (discharge) and 3.9 V (charge).

Cathode/Anode	Electrolyte	Working	Capacity/Theoretical	Highest-rate	Working		
		voltage	capacity	capacity	Temp.	Year	ref
materials		(V)	(mAh g ⁻¹)	(mAh g ⁻¹)	(°C)		
TiS ₂ / Na-Sn	Na ₃ PS ₄ glass-ceramic	1.17-2.40	95/240	/	25	2012	[1]
			(0.01 C, ~94% after				
			10 cycles)				
NIVD/			84/118				
Na	$Na_3Zr_2Si_2PO_{12}$	2.0-3.6	(10 μA cm ⁻² , 76%	/	80	2013	[2]
INd			after 20 cycles)				
NVP/	No Zr Si DO	0.01.1.0	68/118	32	25	2012	[2]
NVP	1Na ₃ Z1 ₂ S1 ₂ FO ₁₂	0.01-1.9	$(1.2 \ \mu A \ cm^{-2})$	(10 µA cm ⁻²)	23	2013	[2]
NVP/ NVP	Na ₃ Zr ₂ Si ₂ PO ₁₂	0-2.2	100/118	56	200	2014	[3]
			(0.1.C)	(0.5 C, ~45%			
			(0.1 C)	after 20 cycles)			
NEMO/			~135/262	~84			
NTO+LSM	$Na-\beta''-Al_2O_3$	1.0-4.0	(0.05 C, 90% after	(1 C, 90% after 100 cycles)	350	2014	[4]
			100 cycles)				
NCMO/ Na	PEO/NaClO ₄ /TiO ₂	1.25-4.3	49/176	/	60	2015	[5]
			(0.1 C, 92% after 25				
			cycles)				
PAQS/ P(AN-NA)	SCN/NaClO ₄	0.8-2.6	196/268	116 (3 C)	25	2015	[6]
			(0.2 C, 82% after 50				
			cycles)				
NaCrO ₂ / Na	Na ₃ SbS ₄	1.2-3.7	108/250	/	30	2016	[7]
			(50 µA cm ⁻² , 55%				
			after 20 cycles)				
TiS./			80/240				
Na	Na _{2.9375} PS _{3.9375} Cl _{0.0625}	1.2-2.4	(0.1 C, 85% after 10	/	25	2016	[8]
			cycles)				
NNM/	$Na-\beta''-Al_2O_3+$		83/176	~70			
Na	ionic liquid	2.5-3.8	(0.1.C)	(2 C, 74% after	70	2016	[9]
	(PY14FSI)		(0.1 C)	650 cycles)			
S/			170/1165	~50			
Na	$Na_{3.1}Zr_{1.95}Mg_{0.05}Si_2PO_{12}$	0.8-3.6	(1 C, 88% after 100	(5 C)	25	2016	[10]
			cycles)	(3.0)			
NVP/ Na	CPE-NZMSPO	2.5-3.8	106/118	90 (0.5 C)	80	2016	[11]
			(0.1 C, ~85% after				
			120 cycles)	(0.0 0)			
NaTi ₂ (PO ₄) ₃ / Na		1.5-2.5	121/132	60 (0.5 C)			
	Na-β"-Al ₂ O ₃		(0.1 C, 82% after 50		25	2016	[12]
			cycles)	(
				96			
NVP/	PEO/NaClO ₄ /Al ₂ O ₃	2.3-3.9	107.5/118	(2 C*, 88%	80	2017	This work
Na			(0.2 C*)	after 1000			
				cycles)			

Table S1 Electrochemical properties and cycling performances for all-solid-state sodium ion batteries

 using different electrode materials and solid electrolytes in the recent five years.

* In this work, the current density was set to 0.2 C and 2 C, which is equivalent to 23 μ A cm⁻² and 230 μ A cm⁻² respectively.



Fig. S1 SEM image of NVP-S with low magnification.



Fig. S2 XRD patterns of NVP-F precursor and NVP-S precursor.



Fig. S3 TG analysis of as-synthesized NVP-F and NVP-S.



Fig. S4 Ionic conductivity of NaClO₄/PEO/Al₂O₃ membrane of different EO : Na ratios.



Fig. S5 Ionic conductivity of NaClO₄/PEO/Al₂O₃ membrane of different contents of Al₂O₃.



Fig. S6 Cyclic voltammograms (CV) of NVP-F and NVP-S at a scan rate of 0.1 mV s⁻¹ in a voltage range of 2.3–3.9 V.



Fig. S7 Nitrogen adsorption-desorption isotherms of (a) NVP-F and (b) NVP-S.



Fig. S8 Rate performances of NVP-F and NVP-S cells using liquid electrolytes.



Fig. S9 Charge-discharge curves at the C-rate of 2 C of long-term cycling tests of (a) NVP-F and (b) NVP-S.



Fig. S10 Performances of all-solid-state batteries with different cathode materials loading:(a) for NVP-S cathode, (b) for NVP-F cathode.

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