Supporting Information

Stable cycling of Na metal anode in carbonate electrolyte

Shiyang Wang,^a Wenbin Cai,^a Zhihao Sun,^a Fanyang Huang,^a Yulin Jie,^a Yang Liu,^a Yawei Chen,^a Bo Peng,^a Ruiguo Cao,^a Genqiang Zhang^a and Shuhong Jiao^{*a}

^a Hefei National Laboratory for Physical Science at the Microscale, CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China

E-mail: jiaosh@ustc.edu.cn

Experimental Section

Material

Sodium hexafluoroarsenate (NaAsF₆) and bis(trifluoromethane)sulfonimide sodium (NaTFSI) were purchased from Alfa Aesar and DoDo chem respectively, all the salts were dried at 100 $^{\circ}$ C over 12 hours before use. Fluoroethylene carbonate (FEC) was obtained from Zhuhai Smoothway Electronic Materials Co., Ltd. Aluminum foil and Na metal were purchased from MTI HF-Kejing and Sinopharm respectively. Glass fiber GF/D was obtained from Whatman.

Characterization

All the batteries were measured on the CT-3000n (Neware battery testing system). CV experiment was carried out on electrochemical workstation (CHI660, Chenhua Instruments Co.,Shanghai). Na surface morphology was characterized by FEI Apero with the accelerating voltage of 2 kV. For XPS characterization, Na||Al cell with hollow PTFE as the separator was assembled with 0.5 mAh cm⁻² of Na metal plated at 0.25 mA cm⁻², then the cycled Na||Al cell was dissembled to obtained the SEI covered Na/Al electrode. The electrode was washed by DMC 3 times and then characterized by ESCALAB 250 without air exposure. Depth profiling after 3 and 6 min were done by Ar ion sputtering at 2 kV over a 2 x 2 mm area. Raman experiment was carried out on Renishaw inVia Raman Microscope.

Electrochemical measurement

Na||Al cell was assembled using Al foil as the cathode and Na foil as the anode with one piece of glass fiber as the separator. In order to exclude the influence of glass fiber, hollow PTFE was used to replace the glass fiber in the Na||Al cells for XPS characterization. The interfacial stability of the Na surface was evaluated by the symmetric Na||Na cell consisted of two pieces of Na foil separated by a piece of glass fiber.



Fig. S1 Cycling performance of the Na||Al cells using the electrolyte with or without 0.75 wt% NaAsF₆ with a fix areal capacity of 0.5 mAh cm⁻² at 0.25 mA cm⁻².



Fig. S2 Cycling performance of the Na||Al cells using the electrolyte with or without 0.75 wt% NaAsF₆ with a fix areal capacity of 0.5 mAh cm⁻² at 0.5 mA cm⁻².



Fig. S3 Raman spectra of the electrolyte with and without 0.75 wt% NaAsF $_{6}$.



Fig. S4 Coulombic efficiency of the Na||Al cells with different amount of the additive cycling at 0.25 mA cm⁻² with an areal capacity of 0.5 mAh cm⁻².



Fig. S5 Nucleation overpotential of the Na||Al cells using the electrolytes with different amount of the additive at 1st cycle. The current density is 0.25 mA cm⁻².



Fig. S6 Growth overpotential of the Na||Al cells using the electrolytes with different amount of the additive at 1st cycle. The current density is 0.25 mA cm⁻².



Fig. S7 Voltage-capacity profiles of the Na||Al cells using various electrolytes at the 1st cycle with a current density of 0.25 mA cm⁻².



Fig. S8 SEM images of the Na anode after 1 cycle at the plating state with the current density of 0.1 mA cm⁻² cycled (a) with or (b) without NaAsF₆.



Fig. S9 Electrochemical performance of $Na_3V_2(PO_4)_3$ | Na full cell with or without 0.75 wt% $NaAsF_6$ cycling at 1 C.



Fig. S10 F atomic ratio of the SEI formed in the electrolyte with or without 0.75 wt% NaAsF₆.



Fig. S11 As $2p_{3/2}$ XPS spectra of the SEI formed on the Na surface using 1 M NaTFSI/FEC without NaAsF₆.

Table S1 Summary of average CE and cycle number of Na metal in carbonatebased electrolyte reported in Figure 1d.

No.	Electrolyte formula	Current density	Discharge	CE	Cycle	References
		(mA cm ⁻²)	capacity		number	
			(mAh cm ⁻²)			
1	1 M NaPF ₆ /PC	0.057	0.336	<20%	10	Sci. Rep., 2016, 6, 22406
2	1 M NaPF ₆ -EC/DMC	0.5	1	<20%	25	ACS Cent. Sci., 2015, 1, 449
3	1 M NaClO ₄ -EC/PC	1	1	<30%	50	Chem. Commun., 2018, 19, 2381
4	1 M NaFSI-EC/PC	0.28	0.56	<30%	100	ACS Appl. Mater. Interfaces,
						2018, 10, 17, 15270
5	1 M NaPF ₆ -EC/DEC	0.2	NA	<30%	300	Nano Energy, 2016, 30, 825
6	1 M NaFSI-EC/PC + 1	0.28	0.56	~37%	100	ACS Appl. Mater. Interfaces,
	wt% FEC					2018, 10, 17, 15270
7	1 M NaClO ₄ -EC/DMC + 5	1	1	~40%	20	Nano Energy, 2019, 29, 825, 866
	wt% FEC					
8	NaFSI/PC from 10/1 to	0.2	NA	<50%	250	Nano Energy, 2016, 30, 825
	1.5/1 (mole ratio)					
9	1 M NaPF ₆ -EC/PC + 1	0.28	0.56	~90%	15	ACS Appl. Mater. Interfaces,
	wt% FEC					2018, 10, 17, 15270
10	1 M NaClO ₄ -EC/PC/FEC	1	1	<90%	50	Chem. Commun., 2018, 19, 2381
11	1 M NaFSI/FFC	0.28	0.56	~94%	100	ACS Appl. Mater, Interfaces
						2018 10 17 15270
						2010, 10, 17, 13270