Electronic Supplementary Information (ESI)

Tin negative electrodes using an FSA-based ionic liquid electrolyte: Improved performance of potassium secondary batteries

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Experimental Details

K[FSA] (purity > 99%; supplied from Nippon Shokubai Co., Ltd.) and [C_3C_1pyrr][FSA] (> 99.9%; Kanto Chemical Co., Inc.) were dried under vacuum at 333 K or above. Tin powder (Sigma-Aldrich, Inc.) and acetylene black (Strem Chemicals, Inc.) was used as received. The electrochemical measurements were conducted using 2032-type coin cells and electrochemical measurement apparatuses (HZ-Pro, Hokuto Denko Corp., or VSP, Bio-Logic Co.). In the coin cells, Sn/AB/PAI electrodes and potassium metal were used as working and counter electrodes, respectively. A two-ply glass-fiber filter paper (Whatman, GF/A, 260 mm) was used as a separator. The working electrodes and separator were vacuum-impregnated with the K[FSA]–[C_3C_1pyrr][FSA] electrolyte prior to the test.

Galvanostatic intermittent titration technique (GITT) was employed according to the following procedure:

1. Galvanostatic electrolysis was conducted at a current density of 10 mAh $(g\text{-}Sn)^{-1}$ for 1 h (*i.e.*, 10 mAh $(g\text{-}Sn)^{-1}$). If the cell voltage reaches −0.1 V (charging) and +1.5 V (discharging), move onto step 2 immediately.
2. The open circuit potential was monitored, and the potential after 3 hours was regarded as the equilibrium value.

3. Steps 1 and 2 were repeated 30 times in total.

To identify the existing phases of the charged Sn/AB/PAI electrode, X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer (Ultima IV, Rigaku Co.; Cu-Kα radiation (λ = 0.15418 nm)) equipped with a 1D high-speed detector (D/teX Ultra, Rigaku Co.) with a nickel filter. The surface of the Sn/AB/PAI electrodes were observed with a field emission scanning electron microscope (FE-SEM; SU-6600, Hitachi). Before these analyses, the electrochemical cells were disassembled and the remaining electrolytes in Sn/AB/PAI electrodes were removed by soaking the samples in dehydrated and deoxidized tetrahydrofuran (water content < 10 ppm, oxygen content < 1 ppm; Wako Pure Chemical Industries, Ltd.). All the reagents were handled in the argon-filled glovebox. The samples were transferred to the X-ray diffractometer and a field emission scanning electron microscope without air exposure.

Table S1 Reported K–Sn alloy phases and the corresponding capacities, compositions, and molar volumes.

Phase	Capacity / mAh $(g\text{-}Sn)^{-1}$	Composition x (in K_xSn)	Molar volume / cm^3 $(mol\text{-}Sn)^{-1}$	Ref.
Sn	0	0	16.29	[a]
K_8Sn_{46}	39	0.17	22.79	[b]
K_6Sn_{25}*	54	0.24	25.61	[c]
K_4Sn_9*	100	0.44	32.67	[d]
KSn_2**	113	0.50	N.A.	[a]
K_2Sn_3**	151	0.67	N.A.	[a]
KSn	226	1.00	45.58	[e]
K_2Sn**	452	2.00	N.A.	[a]

* The phase is not shown in the K–Sn phase diagram [a].

** Crystal structure is unknown.

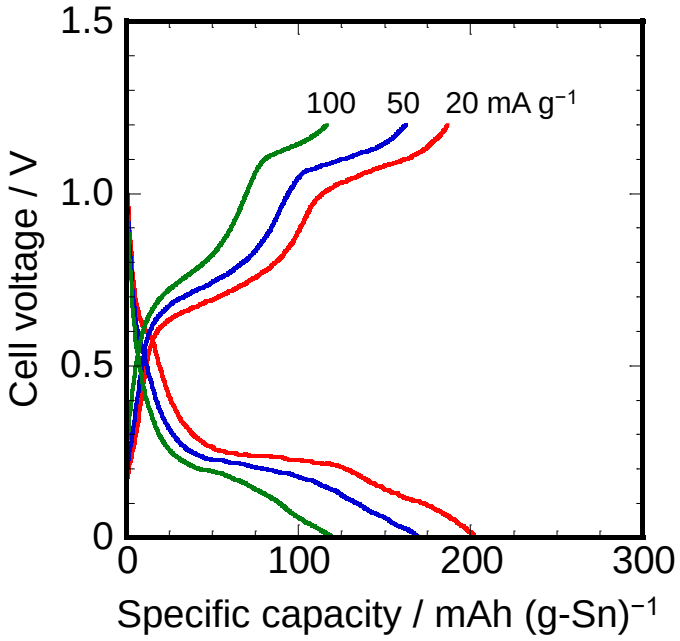

Fig. S1 Rate capability of the Sn/AB/PAI electrode in K[FSA]–[C_3C_1pyrr][FSA] ionic liquid electrolyte at 298 K. Charge–discharge rates: 20, 50, and 100 mA $(g\text{-}Sn)^{-1}$.

The Sn/AB/PAI electrode exhibited the discharge capacities of 187, 162, and 117 mAh $(g\text{-}Sn)^{-1}$ at charge–discharge rates of 20, 50, and 100 mA $(g\text{-}Sn)^{-1}$, respectively.

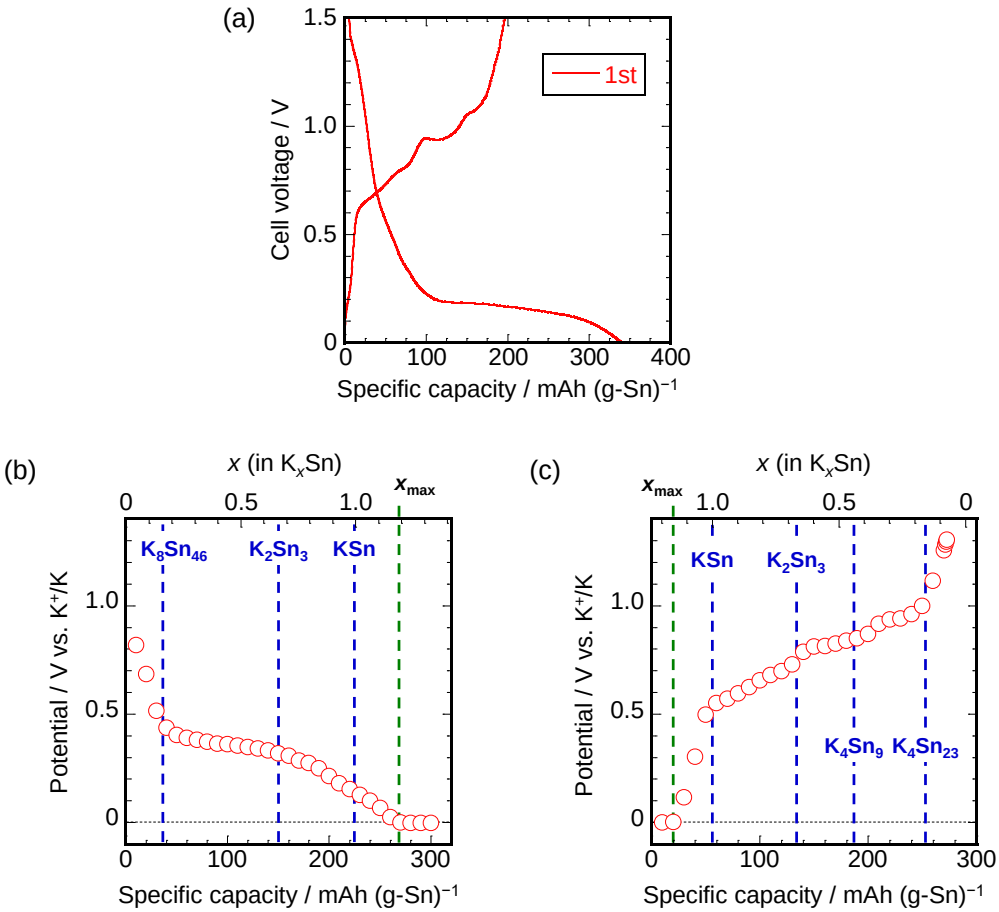

Fig. S2 (a) Initial charge–discharge curves of the Sn/AB/PAI electrode in K[FSA]–[C_3C_1pyrr][FSA] ionic liquid electrolyte at 298 K. Charge–discharge rate: 20 mA $(g\text{-Sn})^{-1}$. Subsequent GITT plots for (b) charging and (c) discharging processes in the 2nd cycle.

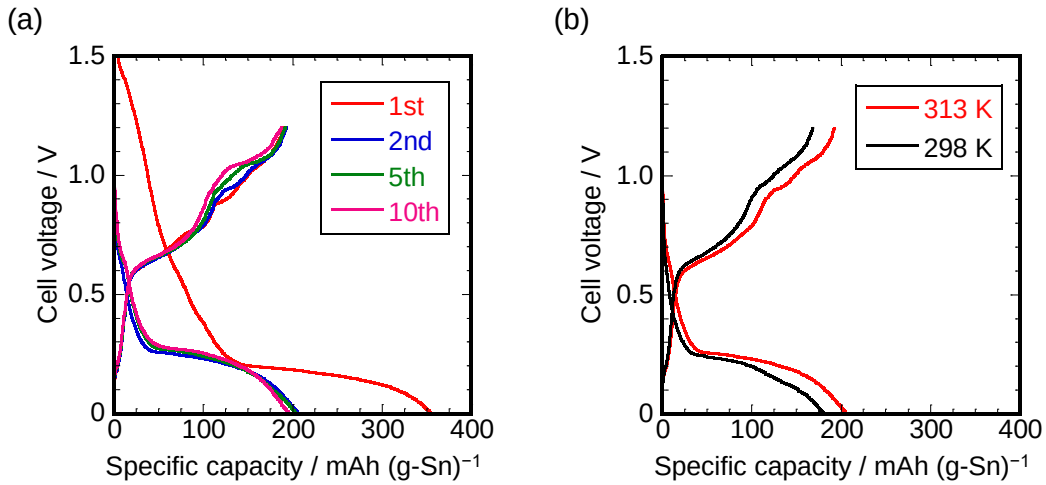

Fig. S3 (a) Charge–discharge curves of the Sn/AB/PAI electrode in K[FSA]–[C_3C_1pyrr][FSA] ionic liquid electrolyte for 10 cycles at 313 K. (b) A comparison of charge–discharge curves in the 2nd cycle at 298 K and 313 K. Charge–discharge rate: 20 mA (g-Sn)$^{-1}$.

References

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