

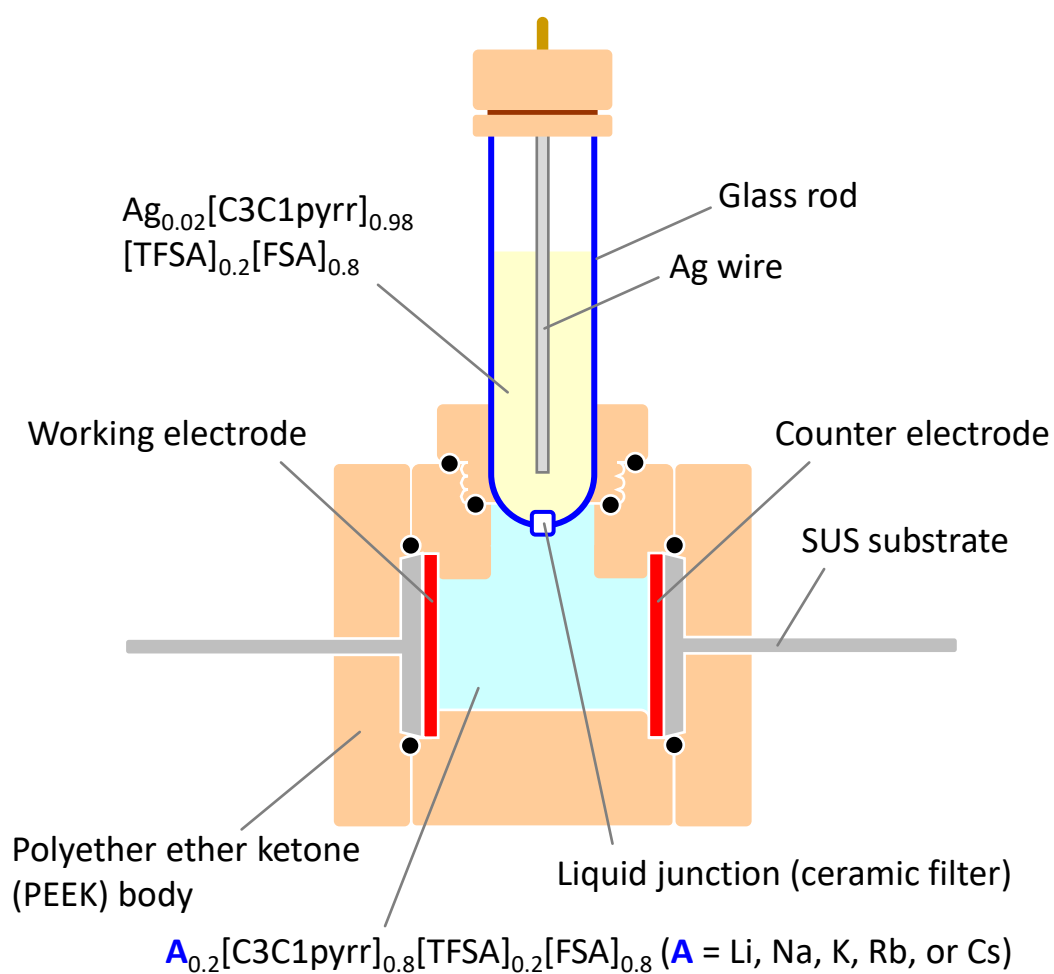
## **Electrochemical Intercalation of Rubidium into Graphite, Hard Carbon, and Soft Carbon**

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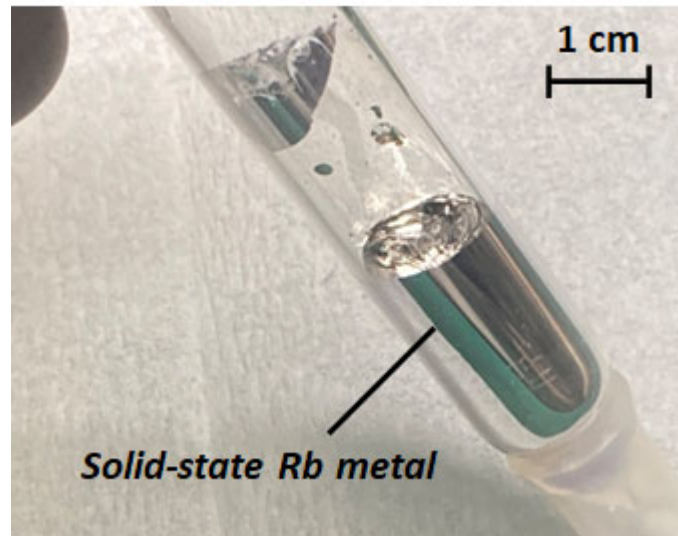
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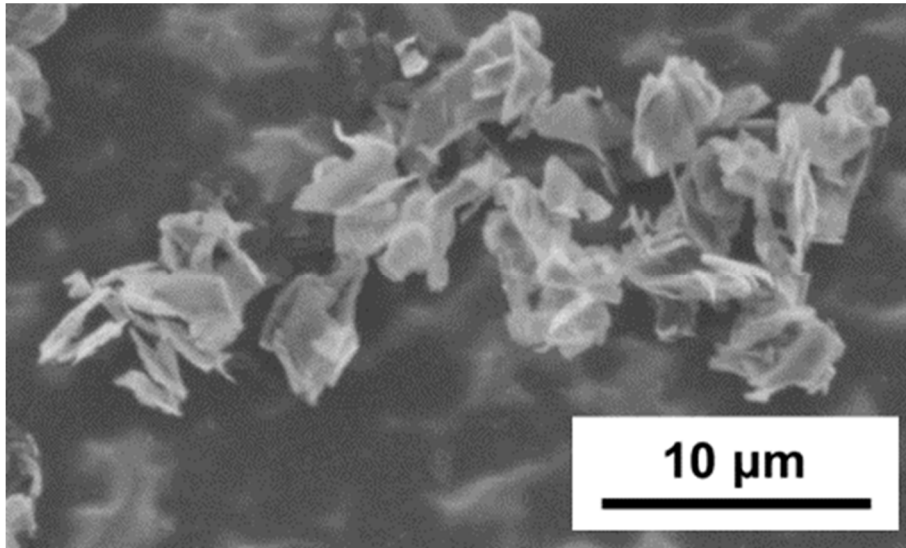
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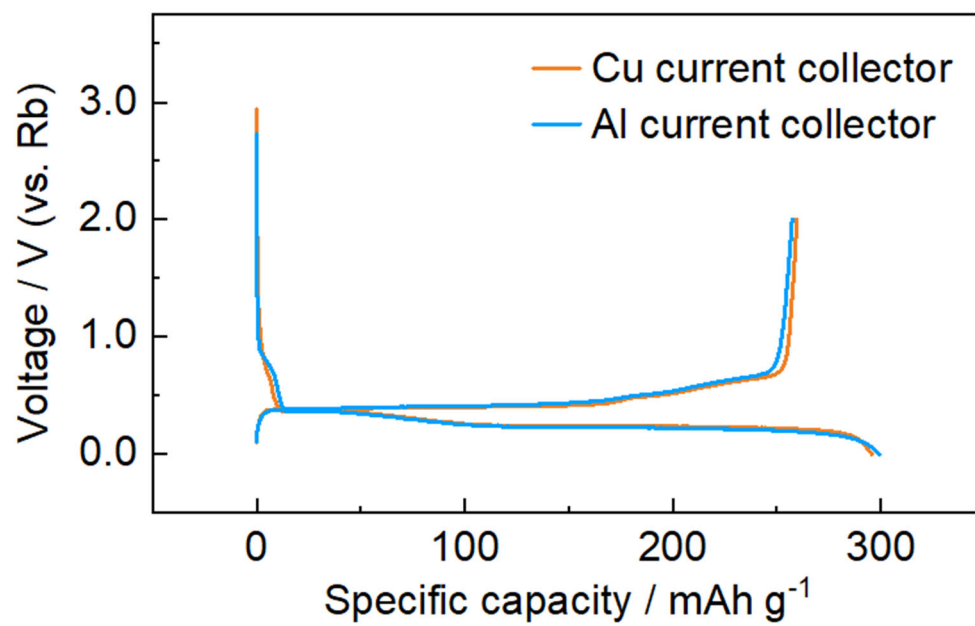
**Fig. S1** Illustration of two-compartment cell used for the measurement of  $\text{A}^+/\text{A}$  electrode potential. Note that non-essential parts are omitted in the illustration. The black circles in the illustration represent cross sections of the O-rings made of EPDM (ethylene propylene diene monomer) rubber that keep the airtightness of the cell.



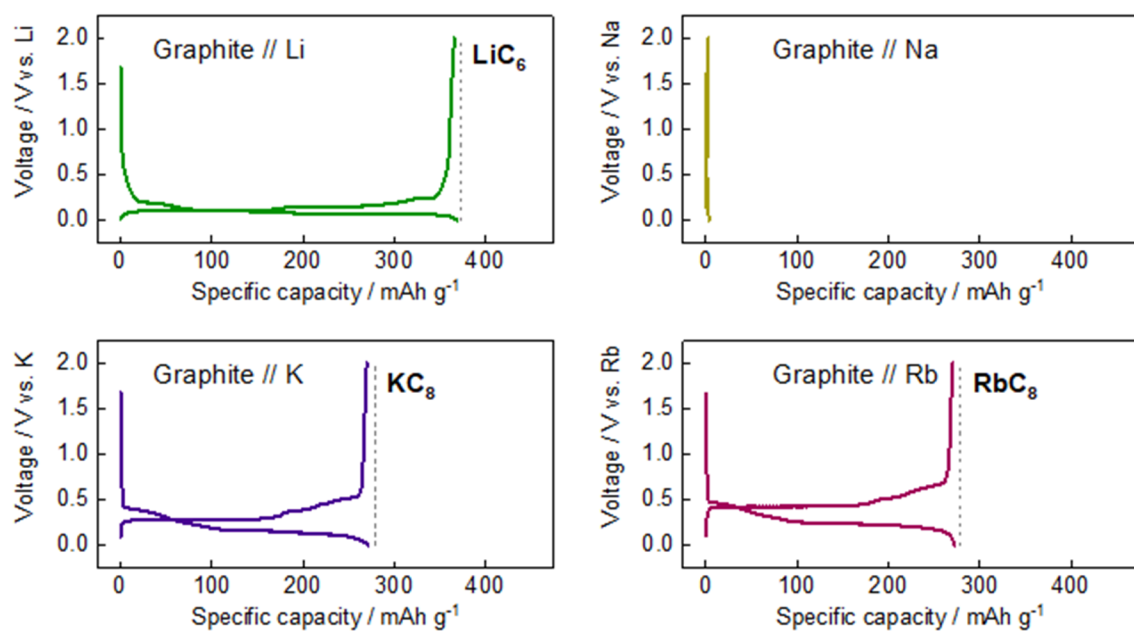
**Fig. S2** Photograph of commercially available Rb metal in a glass ampoule.



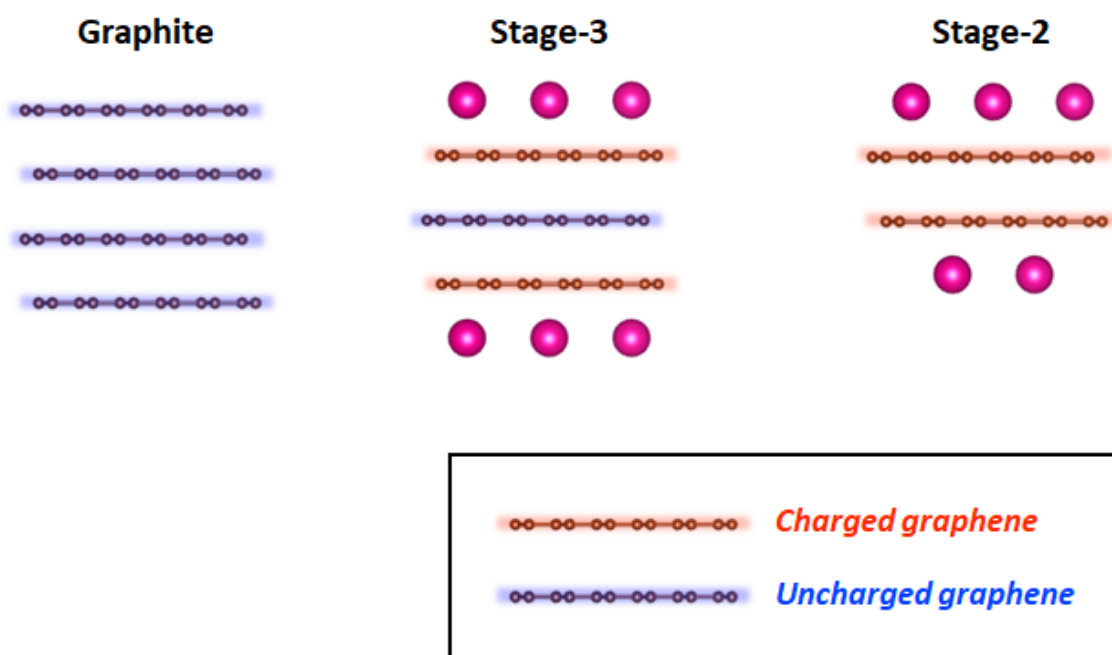
**Fig. S3** Typical SEM image of the natural graphite used in this study.



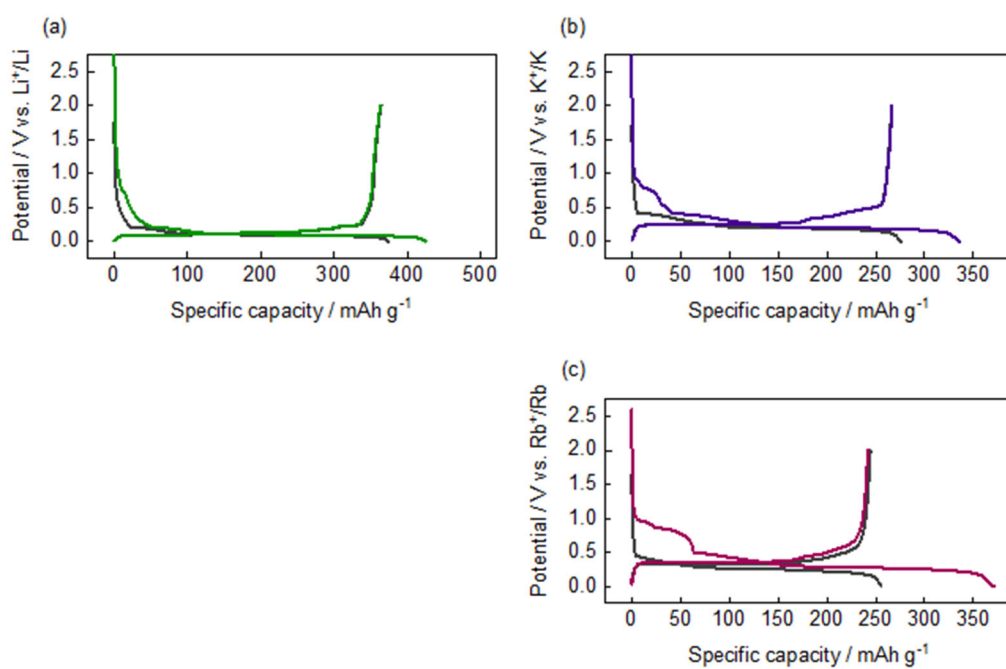
**Fig. S4** Initial galvanostatic reduction–oxidation curves of graphite electrodes with different current collector in Rb cells.



**Fig. S5** Galvanostatic reduction–oxidation curves of graphite electrodes with  $A_2[C_3C_1\text{pyrr}]_{0.8}[\text{TFSA}]_{0.2}[\text{FSA}]_{0.8}$  electrolyte and alkali-metal counter electrode.

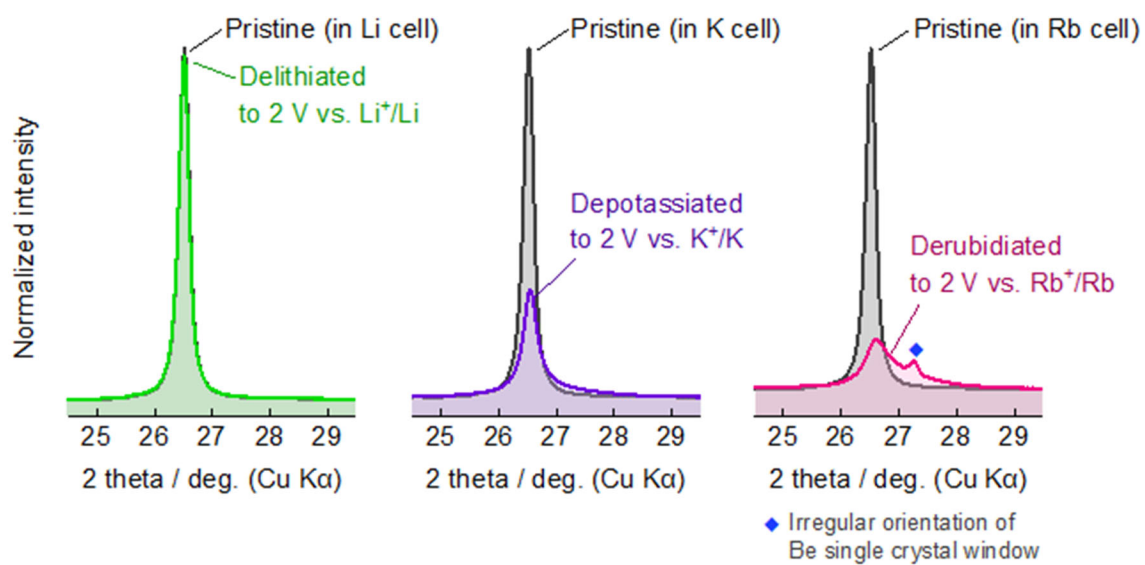


**Fig. S6** Schematic of charged and uncharged graphene in Rb-GICs.

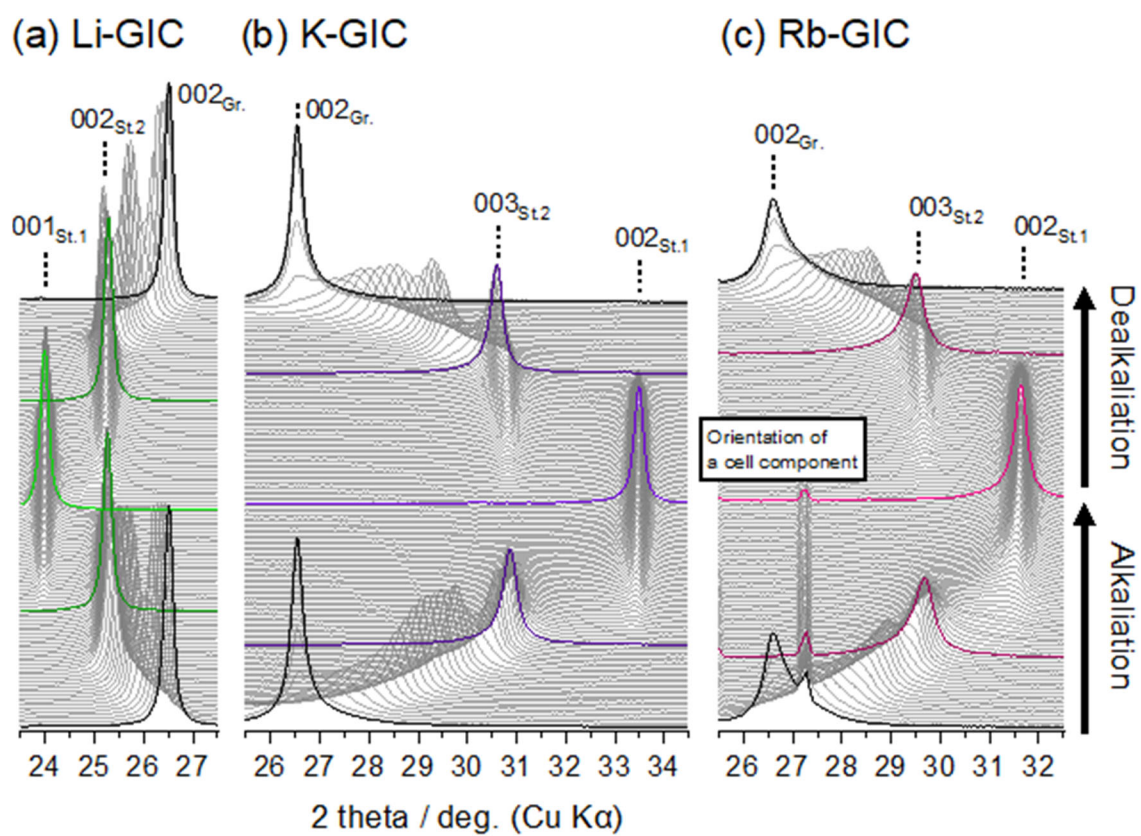


**Fig. S7** Galvanostatic reduction–oxidation curves of graphite electrode in three-electrode (a) Li, (b) K, and (c) Rb cells at current density of  $C/30$ ; samples were further subjected to in-situ XRD analysis.



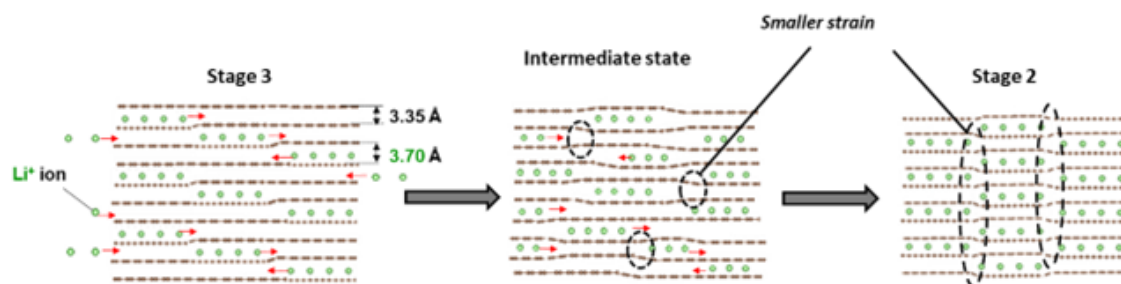


**Fig. S8** In-situ XRD patterns of graphite electrodes in pristine and dealkaliated states at 2 V vs.  $\text{A}^+/\text{A}$  in the 1st cycle.

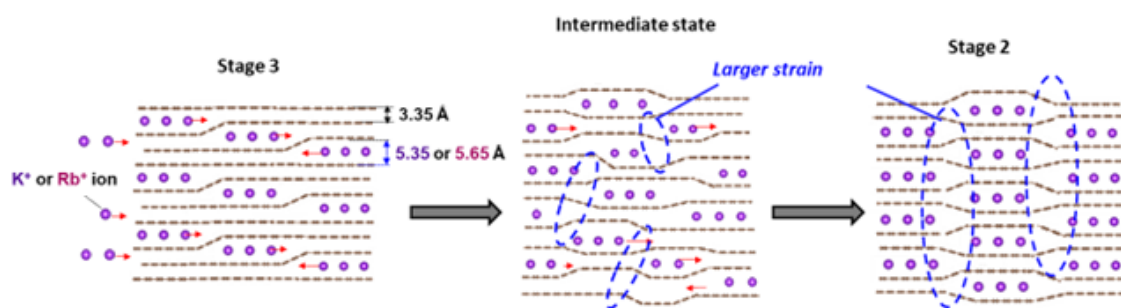


**Fig. S9** Operando XRD patterns of graphite electrodes during 2nd cycle in (a) Li, (b) K, and (c) Rb cells.

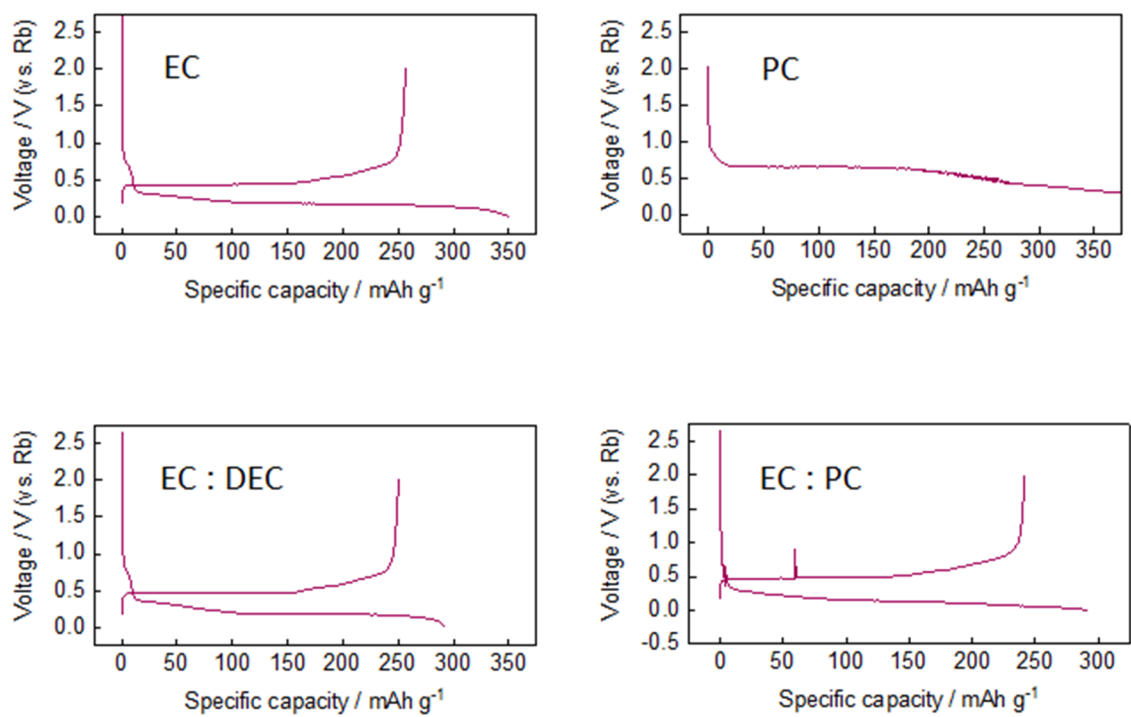
(a) **Li**-intercalation



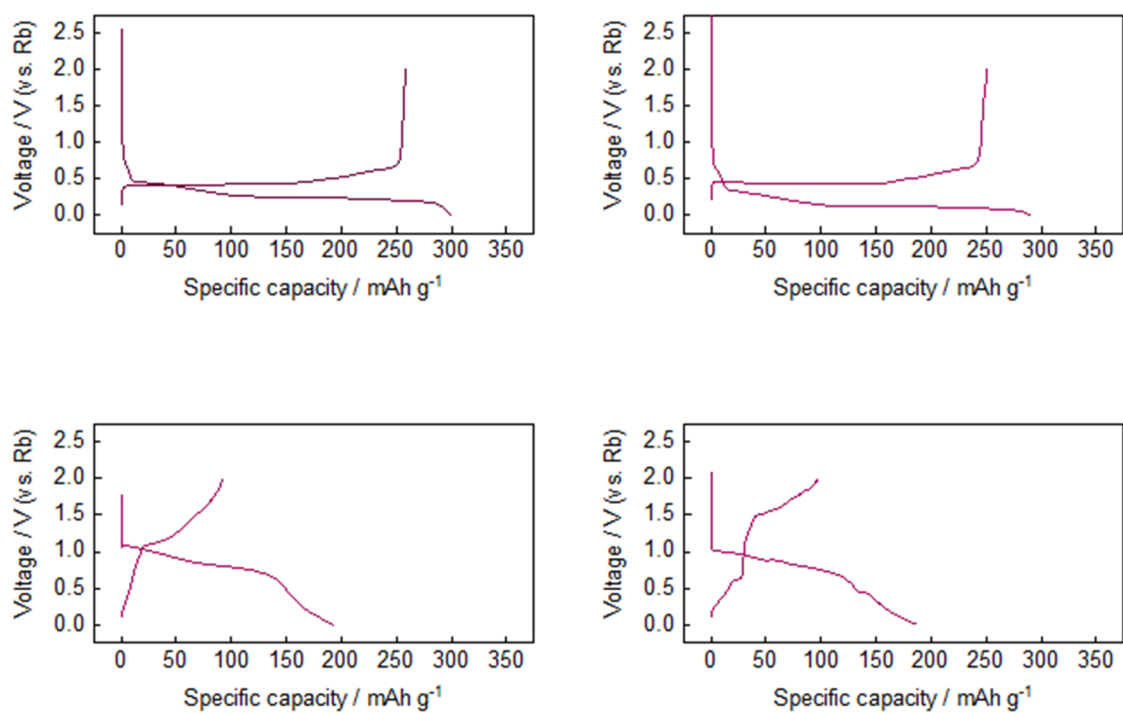
(b) **K, Rb**-intercalation



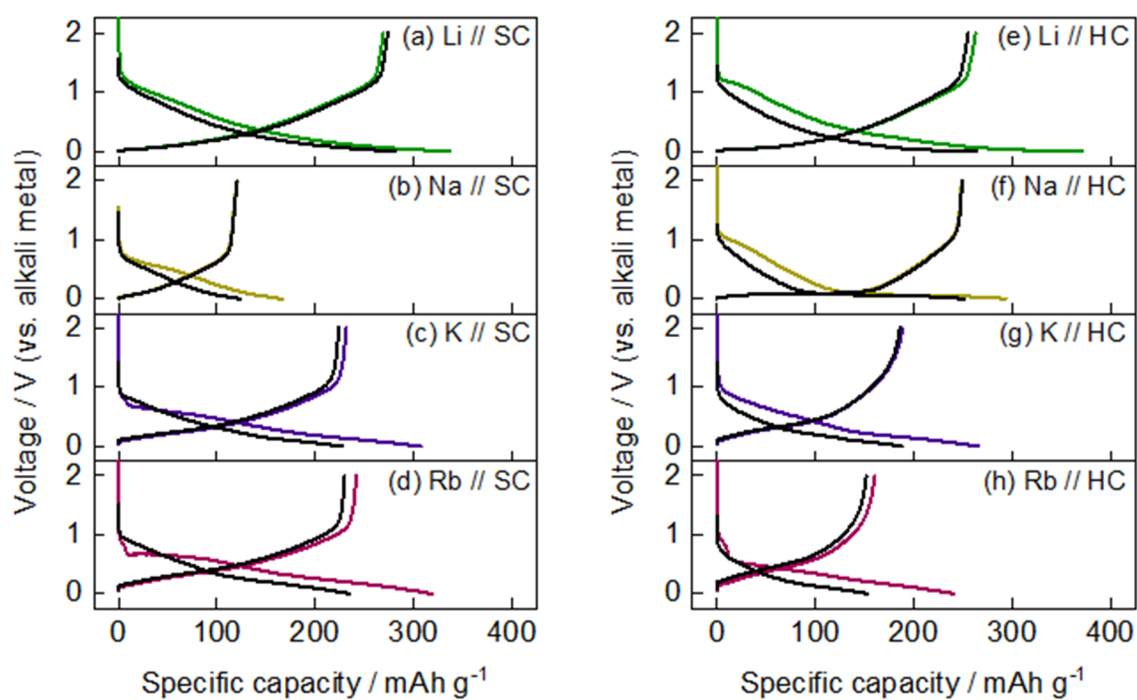
**Fig. S10** Schematic of the assumed phase changes of (a) Li -GICs and (b) larger alkali-metal (K or Rb) -GICs based on the Daumas-Hérold model.



**Fig. S11** Voltage–capacity curves of graphite // Rb cells in (a) 1 mol kg<sup>-1</sup> RbTFSA/EC, (b) 1 mol kg<sup>-1</sup> RbTFSA/PC, (c) 1 mol kg<sup>-1</sup> RbTFSA/EC:DEC, (d) 1 mol kg<sup>-1</sup> RbTFSA/EC:PC.



**Fig. S12** Voltage–capacity curves of graphite // Rb cells in (a) [Rb(G3)][TFSA] (= 5.6 mol kg<sup>-1</sup> RbTFSA/G3), (b) [Rb(G4)][TFSA] (= 4.5 mol kg<sup>-1</sup> RbTFSA/G4), (c) 1 mol kg<sup>-1</sup> RbTFSA/G3, (d) 1 mol kg<sup>-1</sup> RbTFSA/G4.



**Fig. S13** Galvanostatic reduction–oxidation curves of (a) Li // SC, (b) Na // SC, (c) K // SC, (d) Rb // SC, (e) Li // HC, (f) Na // HC, (g) K // HC, and (h) Rb // HC cells. 1st and 2nd cycles are indicated by colored and black lines, respectively.