Supporting Information

Nernstian Li⁺ Intercalation into Few-Layer Graphene and its Use for Determination of K⁺ Co-Intercalation Processes

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Figure S1. Intercalation stages notation and PITT titration duration. **a**, Demonstration of position of various alkali ion intercalation stages and their peak notations used in main text. **b**, Based on the level of current, experimental PITT titration duration were applied as 150 s, 240 s, and 300 s for background, FLG to Stage 3, and Stage 3 to Stage 1 regions, respectively.



Figure S2. Demonstration of PITT method. **a**, CV of FLG before and after PITT test. **b**, Comparison of PITT current-potential transient relationship and the CV behavior of FLG. **c**, Zoom in of PITT result showing individual titration curves.



Figure S3. Characterization of Ag^+/Ag reference stability. **a**, Ferrocene (Fc) CVs on 12.5 µm Pt tip working electrode in different ratio Li⁺/TBA⁺ mixtures. The amount of 0.1 M TBAPF₆ added to 1 mL of 0.1 M LiPF₆ were indicated in the figure's caption. **b**, Fc CVs on 12.5 µm Pt tip in different ratio Li⁺/K⁺ mixtures. The amount of 0.1 M KPF₆ added to 1 mL of 0.1 M LiPF₆ were indicated in the figure's caption. **c**, Summary of Fc's formal potential with total amount of TBAPF₆ or KPF₆ added, showing less than 5 mV reference potential shift throughout the whole range. Ferrocene CVs were obtained at scan rate of 50 mVs⁻¹.



Figure S4. Relationship of peak potential and Li⁺/K⁺ Ratio of selected (de-)intercalation peaks in Figure 3d.



Figure S5. Relationship of peak potential and Li⁺ concentration of (de-)intercalation peaks at different Li⁺ concentration with a constant 0.1 M KPF₆ concentration. All solutions are 0.1 M LiBF₄, KPF₆ or LiPF₆ in PC-EC, scan rates are 500 μ Vs⁻¹ (panel **a**) and 250 μ Vs⁻¹ (panel **b**).

Table S1. Fitting results of Figure 3d and Figure S5.

		Ath Intercolation	3 rd	4 th
			Deintercalation	Deintercalation
Slope of region-I ^{<i>a</i>} / mV	500 µVs ⁻¹ (Figure 3d)	85	58	58
	500 µVs ⁻¹ (Figure S5a)	65	66	68
	250 µVs ⁻¹ (Figure S5b)	54	54	57
Slope of region-II ^b / mV	500 µVs ⁻¹ (Figure 3d)	31	32	30
	500 µVs ⁻¹ (Figure S5a)	29	33	29
	250 µVs ⁻¹ (Figure S5b)	28	31	31

^a Region-I: 0 to 2.9 mM Li⁺.

^b Region-II: 2.9 mM to 0.1 M Li⁺.

Calculation of Potential Shift in Li⁺/K⁺ Co-intercalation at Various Conditions

$$xLi^{+} + yK^{+} + (x + y)e^{-} + zC = Li_{x}K_{y}C_{z}$$
(6)

$$E = E^{o} + \frac{0.0592}{(x+y)} log^{[io]} C_{Li}^{x} C_{K}^{y}$$
(S1)

$$E_{shift} = E - E^{o} = \frac{0.0592}{(x+y)} log^{[m]} C_{Li}^{\ x} C_{K}^{\ y}$$
(7)

Table S2. Calculated E_{shift} and Nernstian-slope for $Li^{+}\!/K^{+}$ Co-intercalation

C (M)	С _К (М)	E _{shift} (V)			
C_{Li} (IVI)		x,y = 1,1	x,y = 1,2	x,y = 2,1	
4.98E-04	9.95E-02	-0.127	-0.105	-0.150	
9.90E-04	9.90E-02	-0.119	-0.099	-0.138	
1.96E-03	9.80E-02	-0.110	-0.093	-0.127	
2.91E-03	9.71E-02	-0.105	-0.090	-0.120	
4.76E-03	9.52E-02	-0.099	-0.086	-0.112	
9.09E-03	9.09E-02	-0.091	-0.081	-0.101	
1.67E-02	8.33E-02	-0.085	-0.078	-0.091	
3.33E-02	6.67E-02	-0.079	-0.076	-0.082	
5.00E-02	5.00E-02	-0.077	-0.077	-0.077	
Slope E_{shift} vs. Log C_{Li} (mV/decade)		26	15	37	
\mathbb{R}^2		0.991	0.955	0.998	

Calculation of experimental E_{shift} in Figure 3e

The experimental potential shift calculation applied equation S1 below. Noticing the potential of corresponding Li^+ intercalation peak at $C_{Li} = 1$ M were referred as inner reference for the E_{shift} calculation:

$$E_{shift} = E_{expt} - E_{CLi = 1M}$$
(S2)

In experiments (Figure 3b), maximum concentration of $C_{Li} = 0.1 \text{ M}$ ($C_K = 0 \text{ M}$) was tested. The $E_{CLi=1 \text{ M}}$ were calculated based on equation S2 below:

$$E_{CLi = 1 M} = E_{CLi = 0.1 M} + 0.059 V$$
(S3)

The calculated result is shown in Table S3 and Figure S6 below.

C (M)	Experimental Potential (V vs. Li ⁺ /Li)		E _{shift} (V)				
C_{Li} (IVI)	F-4	B-4	B-3	F-4	B-4	B-3	Average
2.91E-03	0.05	0.104	0.139	-0.102	-0.105	-0.107	-0.105
4.76E-03	0.051	0.11	0.14	-0.101	-0.099	-0.106	-0.102
9.09E-03	0.061	0.123	0.153	-0.091	-0.086	-0.093	-0.090
1.67E-02	0.073	0.126	0.161	-0.079	-0.083	-0.085	-0.082
3.33E-02	0.08	0.136	0.169	-0.072	-0.073	-0.077	-0.074
5.00E-02	0.088	0.142	0.176	-0.064	-0.067	-0.070	-0.067
1.00E-01	0.093	0.15	0.187				
1.00 ^a	0.152	0.209	0.246	1			
Slope	e_E _{shift} vs. Lo	g C _{Li} (mV/de	cade)	31	30	32	31
R ²			0.979	0.985	0.984	0.991	

Table S3. Calculated experimental E_{shift} in Figure 3e and their Nernstian-slopes.

^{*a*} Calculation based on equation S2.



Figure S6. Comparison of calculated experimental E_{shift} and their averages. The E_{shift} of three experimental representative peaks (F-4, B-4, B-3) and their averages are plotted here. The red line and shadowed area indicate the linear regression fitting and 95% Confidence and Prediction band of the average E_{shift} .

System	K ⁺ /Li ⁺ intercalation patterns within the	BE/M atom,	Average atomic charge	
	same layer	eV ^a	K ⁺	Li+
LiC ₈	-Li-	-0.26	-	0.84
KLiC ₁₆	-K-Li-	0.30	0.80	0.91
K ₂ LiC ₂₄	-K ₂ -Li-	0.14	0.81	0.89
K ₃ LiC ₃₂	-K ₃ -Li-	0.07	0.81	0.85
K ₄ LiC ₄₀	-K ₄ -Li-	0.00	0.82	0.88
K5LiC48	-K ₅ -Li-	-0.02	0.81	0.85
K ₆ LiC ₅₆	-K ₆ -Li-	-0.06	0.81	0.87
K7LiC64	-K ₇ -Li-	-0.07	0.82	0.86
K9LiC80	-K9-Li-	-0.09	0.82	0.86
K ₁₄ LiC ₁₂₀	-K ₁₄ -Li-	-0.13	0.82	0.85
K ₁₉ LiC ₁₆₀	-K ₁₉ -Li-	-0.15	0.82	0.86
K24LiC200	-K ₂₄ -Li-	-0.16	0.82	0.86
K29LiC240	-K ₂₉ -Li-	-0.16	-	-
KC ₈	-K-	-0.20	0.82	-

Table S4. DFT calculated average atomic charges of co-intercalated Li^+ and K^+ ions.

^{*a*} w.r.t. Alkali atom (M) in its stable crystal

Intercalation					
	Conditions	Dilute ^a	Concentrated ^a	Total ^b	
Average diffusion coefficient $D(am^2/a)$	K^+	1.9 E-11 ± 4.3 E-12	3.8 E-12 ± 3.2 E-12	1.3 E-11 ± 1.1 E-11	
	$Li^{+}/K^{+} = 1/50$	2.1 E-11 ± 2.3 E-12	$5.6 \text{ E-12} \pm 4.0 \text{ E-12}$	1.5 E-11 ± 1.2 E-11	
	$Li^{+}/K^{+} = 1/10$	2.3 E-11 ± 2.1 E-12	7.3 E-12 ± 5.2 E-12	1.8 E-11 ± 1.7 E-11	
	$Li^{+}/K^{+} = 1/2$	2.4 E-11 ± 1.7 E-12	1.0 E-11 ± 7.5 E-12	1.8 E-11 ± 1.0 E-11	
D (cm /s)	Li ⁺	$4.2 \text{ E-11} \pm 6.0 \text{ E-12}$	1.1 E-11 ± 5.2 E-12	2.6 E-11 ± 1.9 E-11	
	K^+	1	1	1	
D ratios	$Li^{+}/K^{+} = 1/50$	1.2 ± 0.18	1.8 ± 1.0	1.5 ± 0.83	
<i>vs</i> . K ⁺	$Li^{+}/K^{+} = 1/10$	1.3 ± 0.23	2.4 ± 1.6	1.9 ± 1.4	
Dx / D_K	$Li^{+}/K^{+} = 1/2$	1.4 ± 0.29	3.2 ± 2.1	2.4 ± 1.9	
	Li ⁺	2.3 ± 0.38	3.5 ± 1.9	3.0 ± 1.6	
Deintercalation					
	Conditions	Dilute ^a	Concentrated ^a	Total ^b	
Average diffusion coefficient D (cm ² /s)	K^+	1.9 E-11 ± 1.3 E-11	$7.0 \text{ E-12} \pm 6.9 \text{ E-12}$	1.3 E-11 ± 1.1 E-11	
	$Li^{+}/K^{+} = 1/50$	4.5 E-11 ± 1.8 E-11	1.4 E-11 ± 9.7 E-12	2.9 E-11 ± 2.9 E-11	
	$Li^{+}/K^{+} = 1/10$	4.3 E-11 ± 1.5 E-11	2.0 E-11 ± 1.6 E-11	3.1 E-11 ± 3.0 E-11	
	$Li^{+}/K^{+} = 1/2$	$3.4 \text{ E-11} \pm 2.0 \text{ E-11}$	2.1 E-11 ± 1.6 E-11	2.7 E-11 ± 2.1 E-11	
	Li ⁺	5.4 E-11 ± 1.3 E-11	2.7 E-11 ± 2.1 E-11	4.0 E-11 ± 3.3 E-11	
	K^+	1	1	1	
D ratios vs. K ⁺ Dx / D _K	$Li^{+}/K^{+} = 1/50$	2.3 ± 1.1	1.8 ± 0.44	2.1 ± 0.96	
	$Li^{+}/K^{+} = 1/10$	2.4 ± 1.0	2.5 ± 0.64	2.4 ± 1.0	
	$Li^{+}/K^{+} = 1/2$	2.4 ± 1.2	2.8 ± 0.67	2.4 ± 1.2	
	Li ⁺	3 .4 ± 1.9	3.7 ± 0.93	3.4 ± 1.9	

Table S5. Diffusion coefficient analysis of Li^+/K^+ co-intercalation

^{*a*} Definition of dilute and concentrated region can be found in Figure 5c.

^b Total average of diffusion coefficients at all potentials, both dilute and concentrate regions are included.



Figure S7. The ratio of diffusion coefficient at various Li⁺ concentrations *vs*. that of the pure K⁺ system. Diffusion coefficient ratio $R = D_x/D_K$; Li number concentration $N_{Li} = n_{Li} / (n_{Li} + n_K)$. All experiments were tested in 0.1 M LiBF₄, KPF₆ or LiPF₆ in PC-EC, on 4.9 mm² FLG working electrode at 1 mVs⁻¹.



Figure S8. Example calculation method of diffusion coefficient ratio between different co-intercalation system and pristine K⁺ at various stages (merged potentials). The example used here is D_{Li}^+ / D_K^+ , the inserted lines represent the average value of 3.4.