

Supporting Information for
Acceptor-Type Hydroxide Graphite Intercalation Compounds
Electrochemically Formed in High Ionic Strength Solutions

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- **Simulated XRD patterns**

Simulated intensity of XRD patterns was computed as follows,

$$I_{\text{calc}}^{00l} = \sum_j |f_j m_j \exp(2\pi i l z_j)|^2 LPA$$

where f_j is the atomic scattering factor of the j^{th} atomic layer, m_j is the atomic density of the j^{th} layer ($0 < m_j < 1$), z_j is the c -axis position of the j^{th} layer, L is the Lorenz factor, P is polarization factor, and A is absorption factor. We used the following equations to calculate these factors.

$$L = \frac{1}{\sin 2\theta}$$

$$P = \frac{1 + \cos^2(26.6) \times \cos 2\theta}{1 + \cos^2(26.6)}$$

$$A = 1 - \exp\left(-\frac{2\mu t}{\sin \theta}\right)$$

where μ is the absorption coefficient and t is the thickness of the sample. In addition, the atomic scattering factors were calculated by the following equation,

$$f = \sum_{i=1}^4 a_i \exp\left(-\frac{b_i \sin^2 \theta}{\lambda^2}\right) + c$$

where a_i , b_i , and c are the parameters as shown in Table. For the structure analysis, we varied the parameters (m_j and z_j) to compare the simulated and measured XRD intensities.

- **DFT calculation**

DFT calculation was performed using the hybrid density functional theory incorporating the Becke's three parameter exchange with Lee, Yang and Parr's (B3LYP) correlation functional in Gaussian 09 package.¹ A split-valence basis set with polarization and diffuse functions was used (6-31G++(d,p)). The initial position of $\text{OH}^- \cdot 2\text{H}_2\text{O}$ was similar to the previous report,² and the complex structure was fully optimized. After the calculation was converged, a distance between two parallel white lines running in Fig. S3 was calculated, and the distance was used for comparison with XRD simulation.

- **Characterization of the electrolytes**

We measured the ionic conductivities using a two-electrode symmetrical cell with Pt electrodes. Using an aqueous solution of 0.1 M KCl ($\sigma = 12.85 \text{ mS cm}^{-1}$) as a reference, we

evaluated the ionic conductivities based on the results of the electrochemical impedance measurements. The viscosity of the electrolytes was measured with an automatic viscometer (AMVn 1569, Anton Paar).

Table S1. Parameters to calculate the atomic scattering factors

Element	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
C	2.31	20.8439	1.02	10.2075	1.5886	0.5687	0.865	51.6512	0.2156
O	3.0485	13.2771	2.2868	5.7011	1.5463	0.3239	0.867	32.9089	0.2508
H	0.493002	10.5109	0.322912	26.1257	0.140191	3.14236	0.04081	57.7997	0.003038

Table S2. Physicochemical properties of solutions used for electrolytes

Electrolyte	GIC structure			σ [mS cm ⁻¹]	μ [mPa s]	OH ⁻ /H ₂ O molar ratio	H ₂ O/salt molar ratio
	Intercalate	Staging	d_i [nm]				
15 M KOH	OH ⁻ ·2H ₂ O	3	0.70	350	9.2	1 / 2.9	2.9
6.0 M KOH + saturated CH ₃ COOK	OH ⁻ ·2H ₂ O	1	0.69	71	19.0	1 / 8.5	2.1
NaOH-KOH (51:49) molten hydroxide mixture	OH ⁻	6	0.42	1400 (500 K) [*]	2.4 (500 K) [*]	1 / 0.12 ^{**}	0.12

* Value from James A. Plambeck, in A. J. Bard (Ed.) "Encyclopedia of Electrochemistry of the Elements, Fused Salt System", Vol. 10 (Marcel Dekker) p 3, New York 1976.

** Calculated based on the assumption that the half of the water initially present was removed by heating and then the composition of NaOH-KOH-H₂O would be 45-44-11 mol% [Ref. 16].

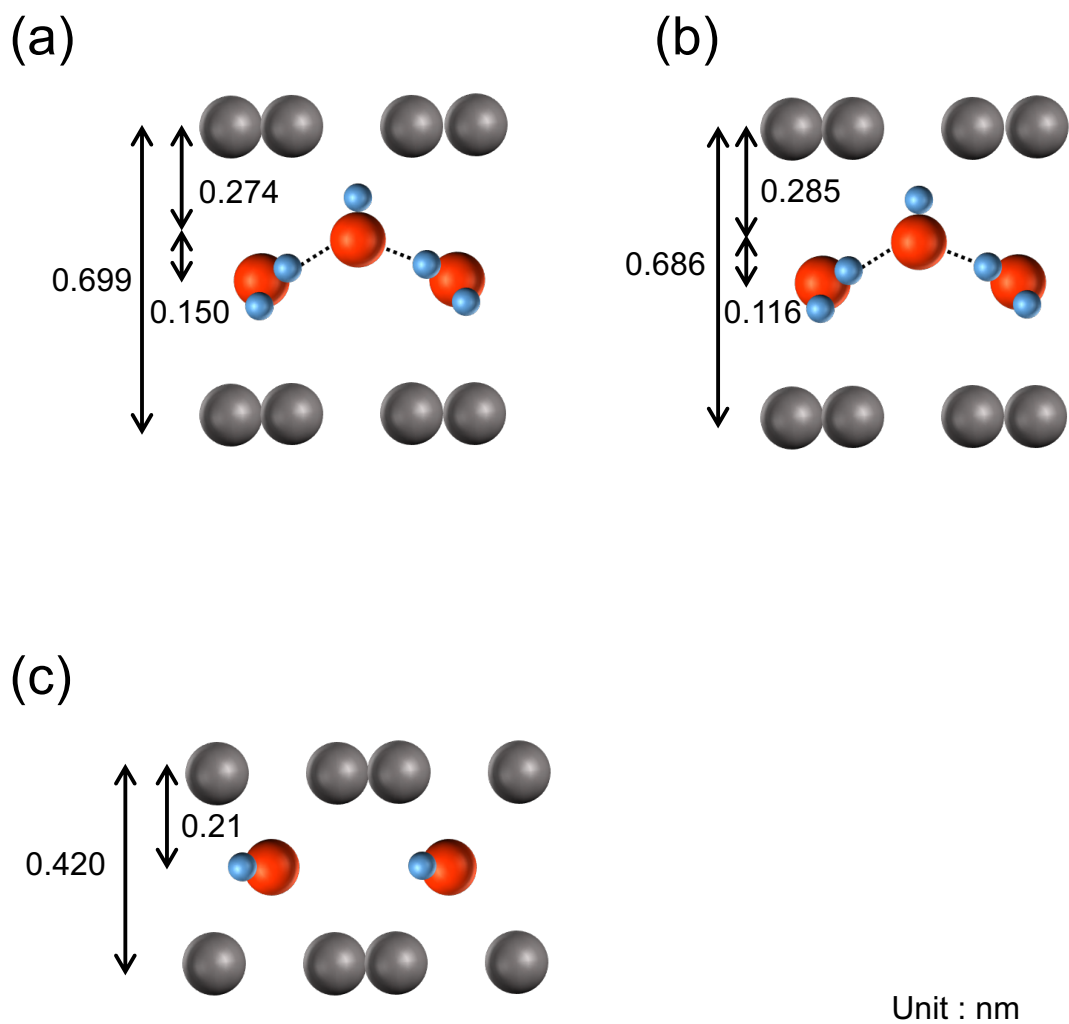


Figure S1. Stacking models of GICs for simulated XRD patterns: (a) 15 M KOH, (b) 6.0 M KOH plus saturated CH_3COOK , and (c) molten salt of NaOH-KOH. Elemental symbols: C (black), O (red), and H (blue).

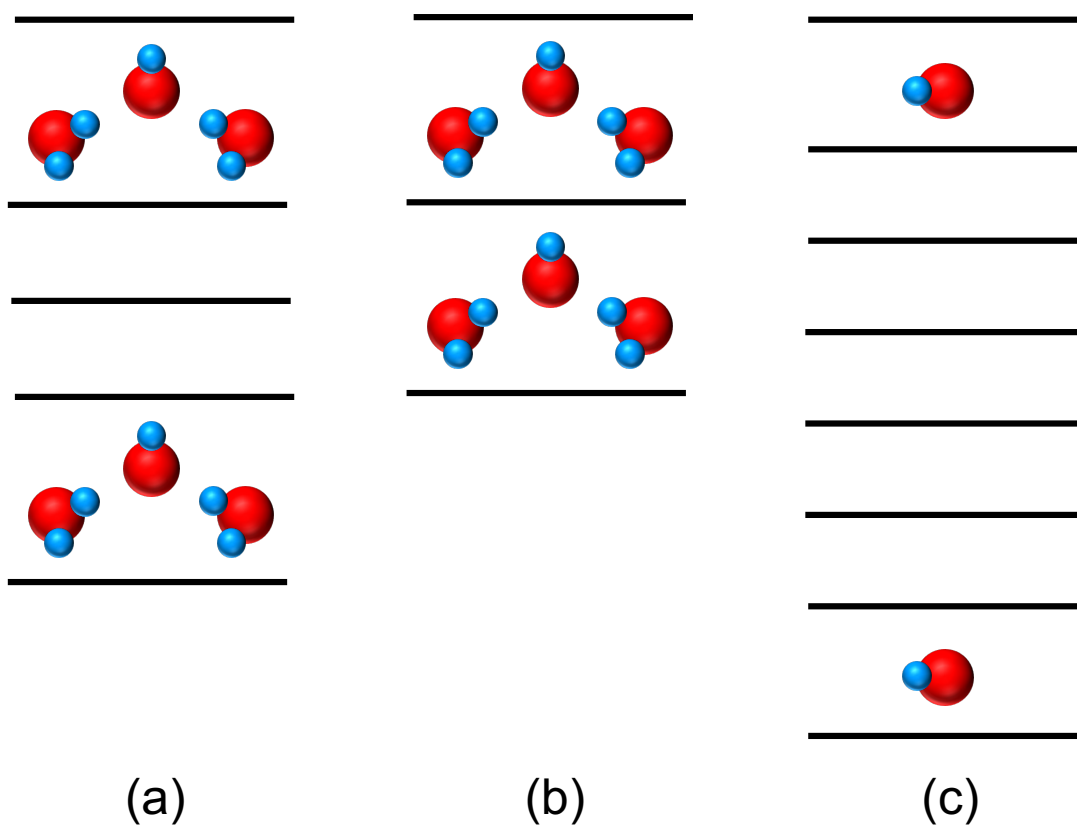


Figure S2. Schematic illustration of GIC staging of (a) stage 3, (b) stage 1, and (c) stage 6. Graphite layers are depicted by black lines.

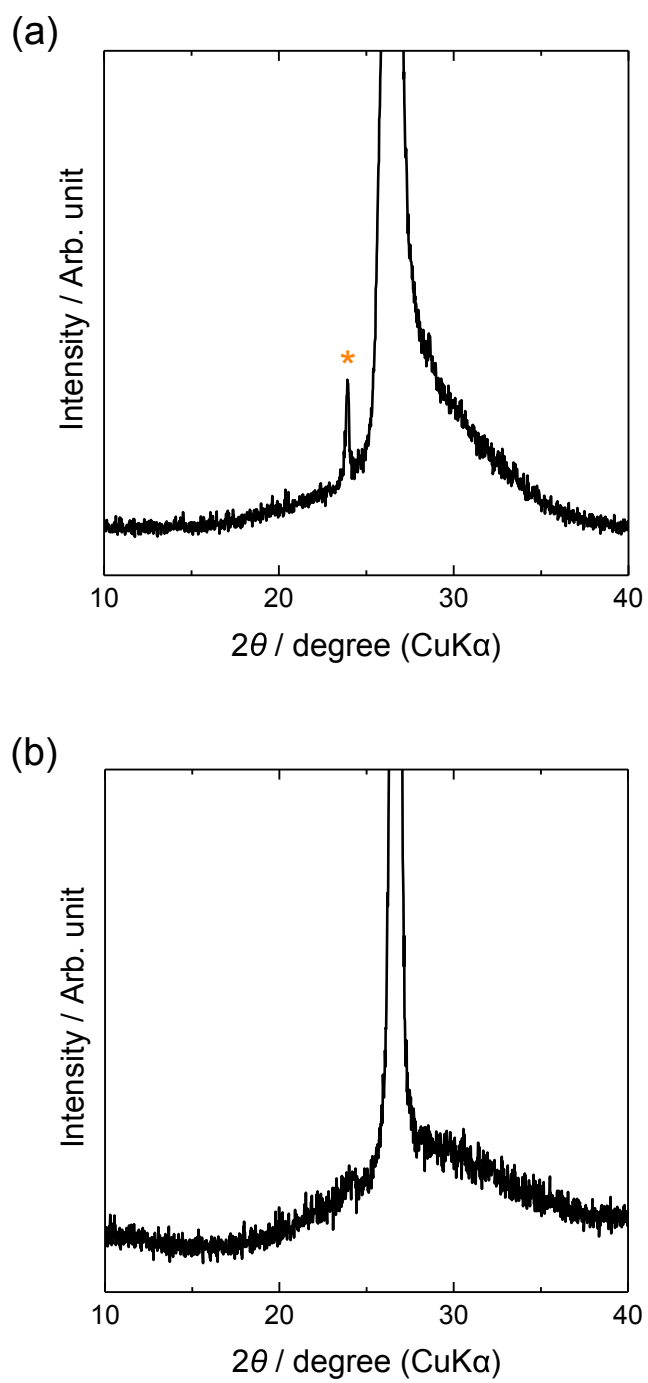


Figure S3. XRD patterns of (a) a pristine graphite sheet and (b) a graphite sheet kept in an aqueous solution of 1 M KOH at 1.1 V (vs. Hg/HgO) for 1 h.

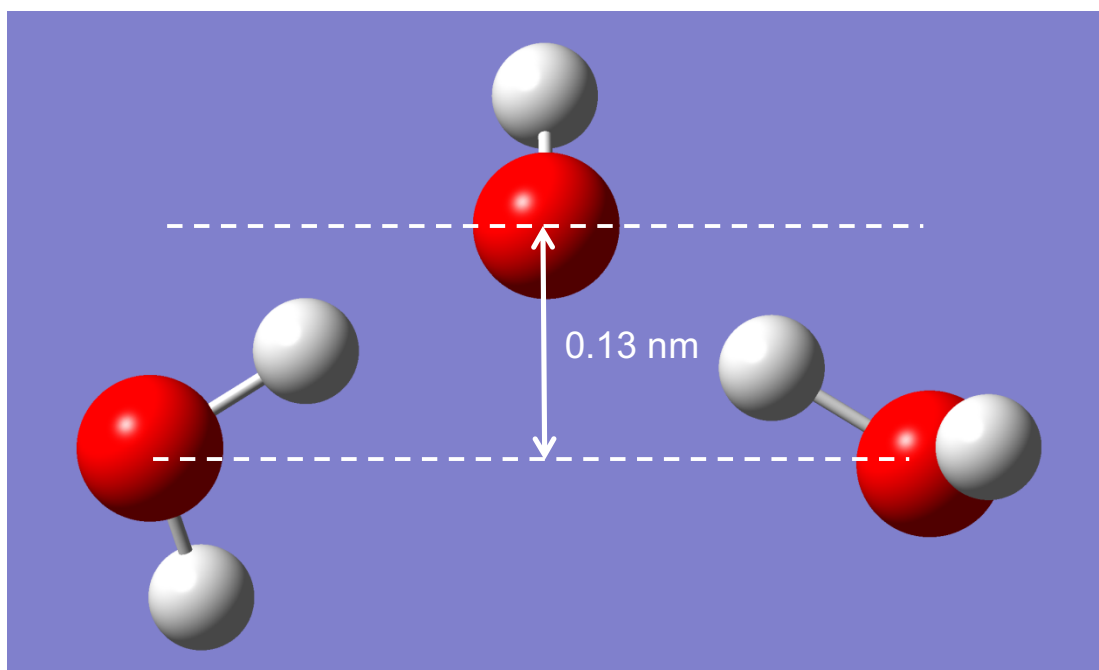


Figure S4. Conformation of an anionic complex $\text{OH}^- \cdot 2\text{H}_2\text{O}$ proposed by DFT calculation.

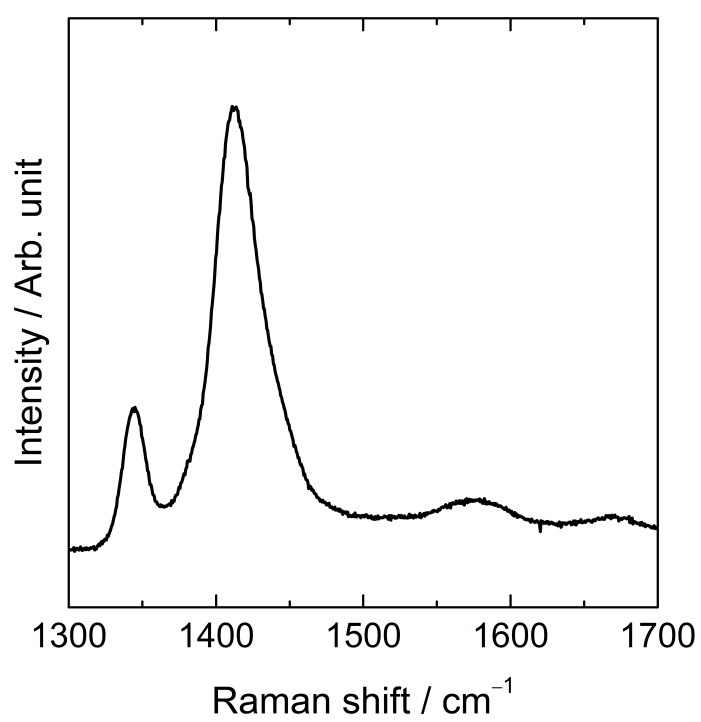


Figure S5. Raman spectrum of an aqueous solution of 6 M KOH plus saturated CH₃COOK.

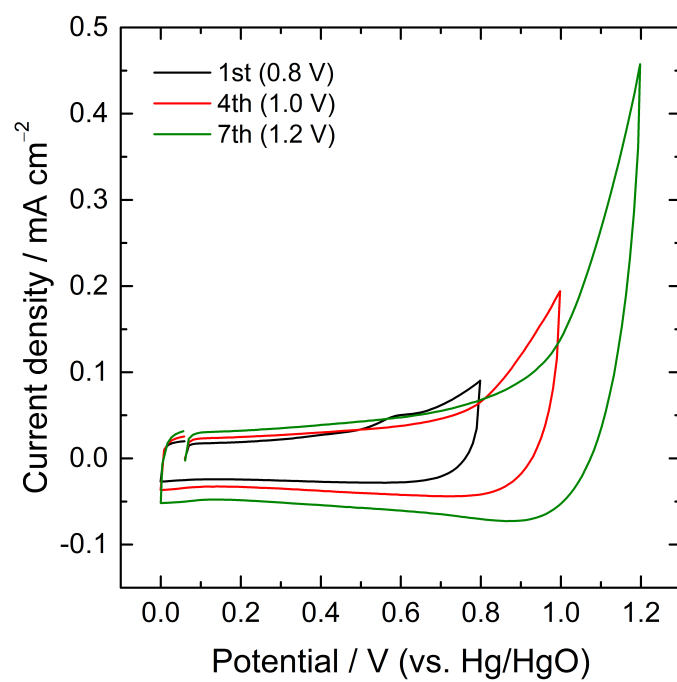


Figure S6. Cyclic voltammograms of graphite sheets in an aqueous solution of saturated CH_3COOK .

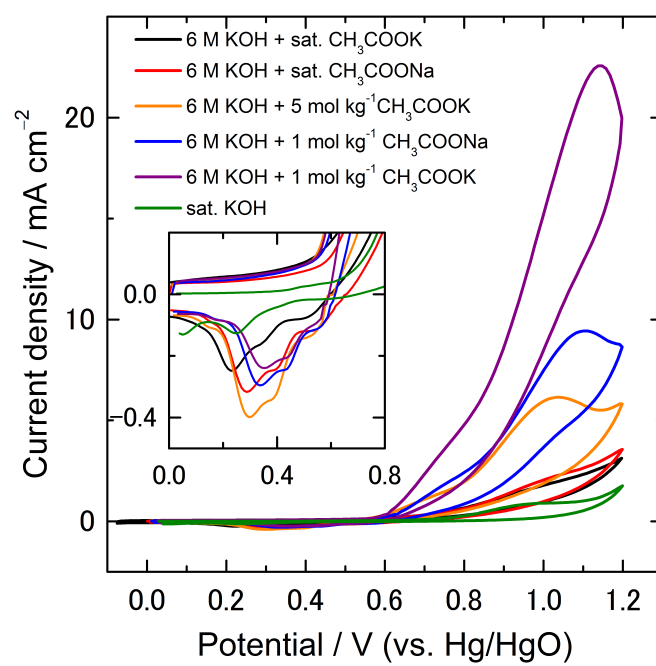


Figure S7. Cyclic voltammograms of graphite sheets in various aqueous solutions.

References

- 1 Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- 2 C.P. Valle and J.J. Novoa, *Chem. Phys. Lett.*, 1997, **269**, 401.