

Supporting information

Mechanism of bulky imidazolium cation storage in dual graphite batteries: A spectroscopic and theoretical investigation

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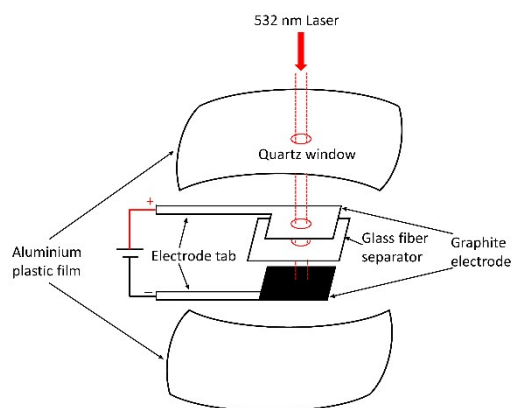


Figure S1. Schematic of the setup for *in-situ* Raman spectroscopy measurement during the charge/discharge cycling of a dual graphite pouch cell using 1,2-dimethyl-3-propylimidazolium chloroaluminate (DMPI⁺)(AlCl₄⁻) electrolyte.

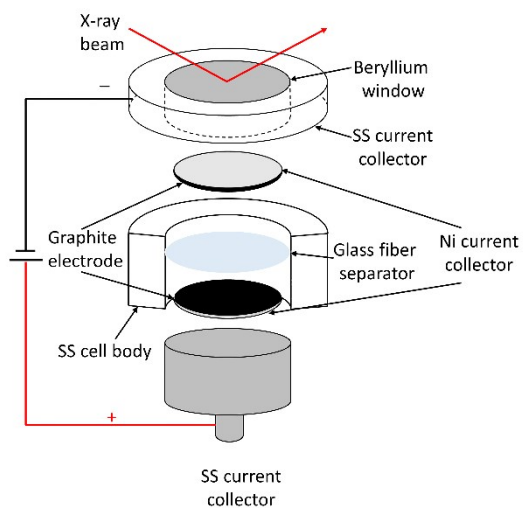


Figure S2. Schematic of the setup for *in-situ* X-Ray diffraction (XRD) characterization during the charge/discharge cycling of a dual graphite cell using 1,2-dimethyl-3-propylimidazolium chloroaluminate (DMPI⁺)(AlCl₄⁻) electrolyte.

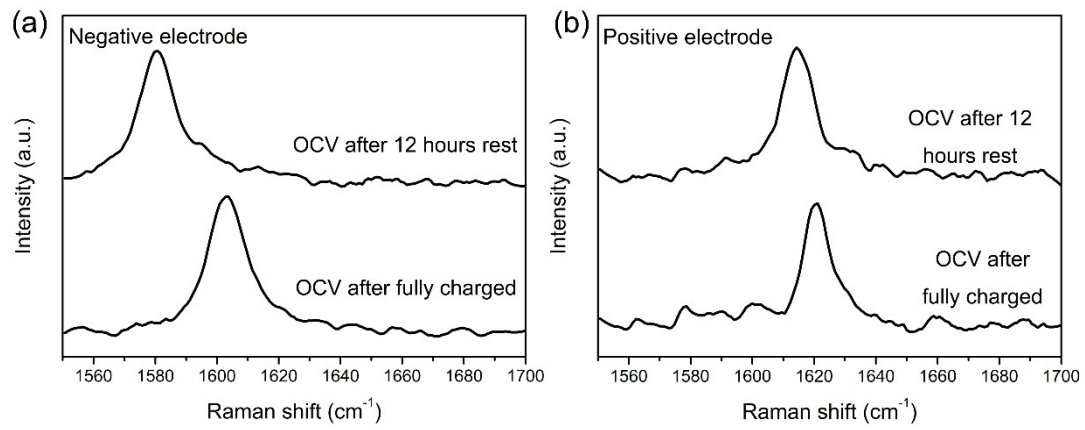


Figure S3. Raman spectra of negative electrode (a) and positive electrode (b) collected under OCV after being fully charged to 4.3V and then 12 hours rest.

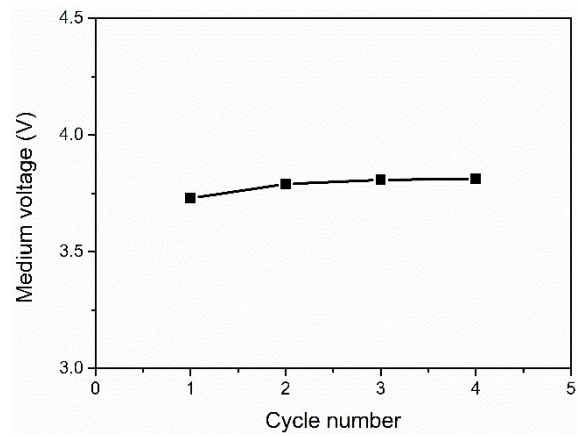


Figure S4. The plot of medium voltage vs. cycles recorded from an *in situ* XRD cell.

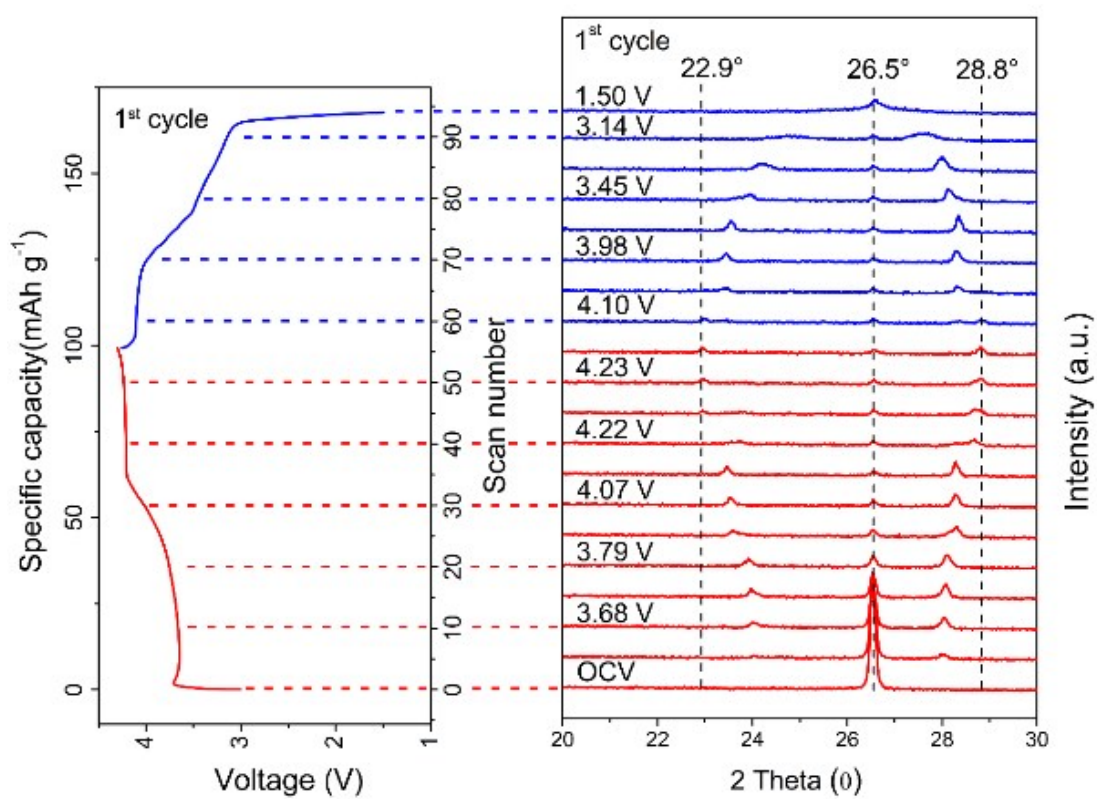


Figure S5. Selected *in-situ* X-Ray diffraction (XRD) spectra of the positive graphite electrode for the 1st charge/discharge cycle of a dual graphite pouch cell using 1,2-dimethyl-3-propylimidazolium chloroaluminate (DMPI⁺)(AlCl₄⁻) electrolyte.

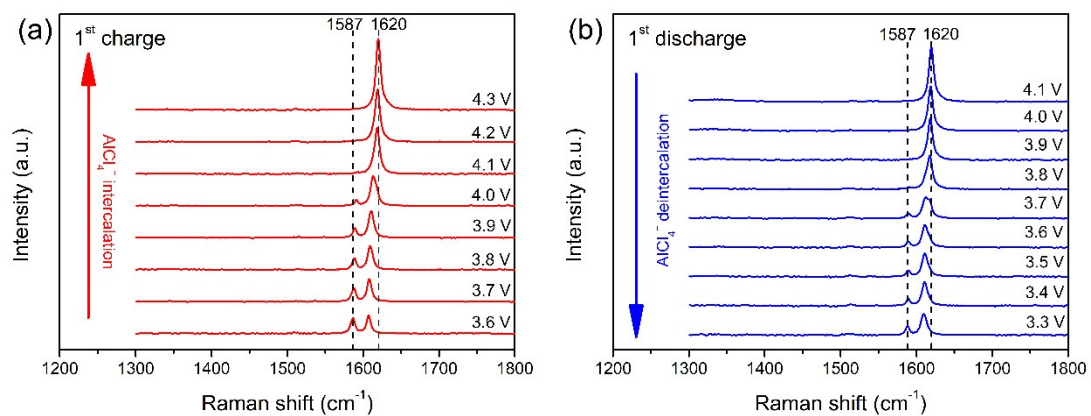


Figure S6. *In-situ* Raman spectra recorded at various fixed voltages of the positive graphite electrode in the 1st cycle during charging (a) and discharging (b) from a dual graphite cell using 1,2-dimethyl-3-propylimidazolium chloroaluminate (DMPI⁺)(AlCl₄⁻) electrolyte.

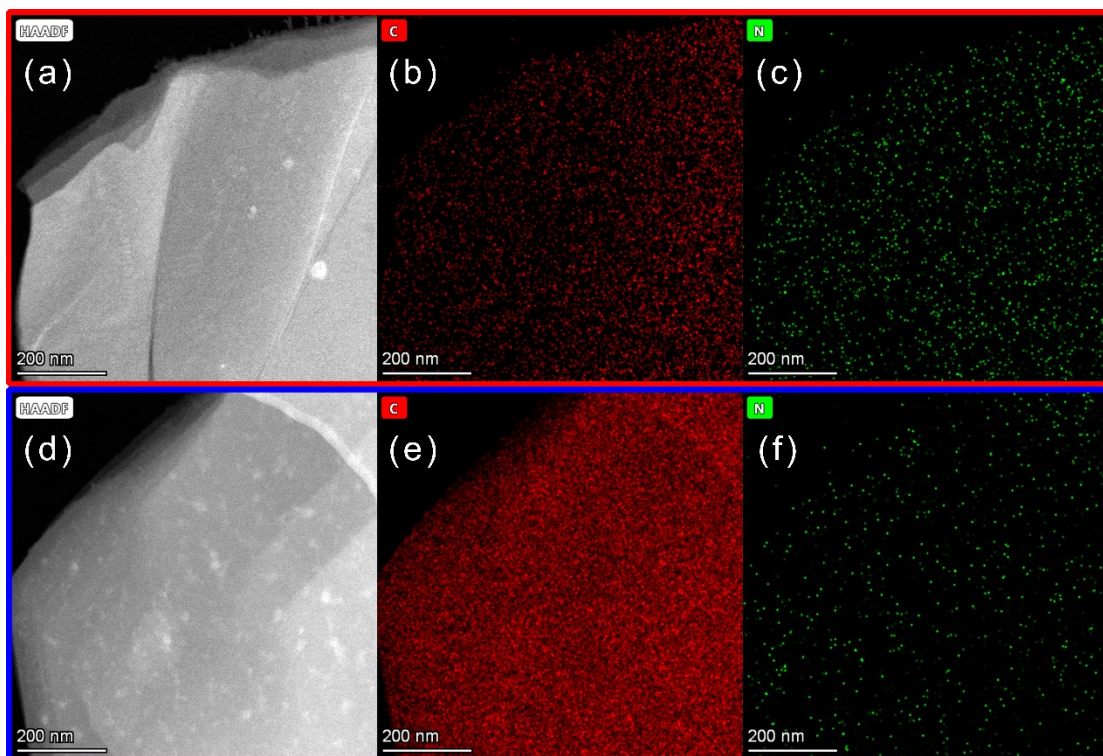


Figure S7. HR-TEM and EDS elemental mapping images for C and N elements of negative GE after being charging to 4.3 V (a-c) and discharging to 1.5 V (d-f), respectively.

The capacitive contribution can be quantitatively estimated using the Trasatti analysis.¹⁻⁴ The dependence between measured voltammetric charges $q(v)$ and scan rate have been erected in the following equation.

$$q(v) = q_{\text{capacitive}} + \alpha(v^{-1/2}) \quad (\text{S1})$$

$$\frac{1}{q(v)} = \frac{1}{q_{\text{total}}} + \alpha(v^{1/2}) \quad (\text{S2})$$

where $q_{\text{capacitive}}$ refers to capacitive charges (both from double layer and pseudocapacitive processes),¹ q_{total} refers to total amount of charges, and α is a constant. The plot of $q(v)$ versus $v^{-1/2}$ is shown in Figure 8(a), when $v \rightarrow \infty$, the electrochemical response depends only on the capacitive charges due to the slow diffusion-controlled behavior, the intercept of the fitting plot (i.e. $q_{\text{capacitive}}$) is calculated to be 83.94 mAh g⁻¹. Besides, The plot of $1/q(v)$ versus $v^{1/2}$ is shown in Figure 8(b), when $v \rightarrow 0$, the electrochemical response has enough time to diffuse, the 1/intercept of the fitting plot (i.e. q_{total}) is calculated to be 95.87 mAh g⁻¹, which agrees with the specific capacity of the full cell. Using the relationship $q_{\text{total}} = q_{\text{capacitive}} + q_{\text{diffusion}}$, diffusion-controlled contribution is calculated to be 11.93 mAh g⁻¹ and the percentage of capacitive contribution is 87.56%.

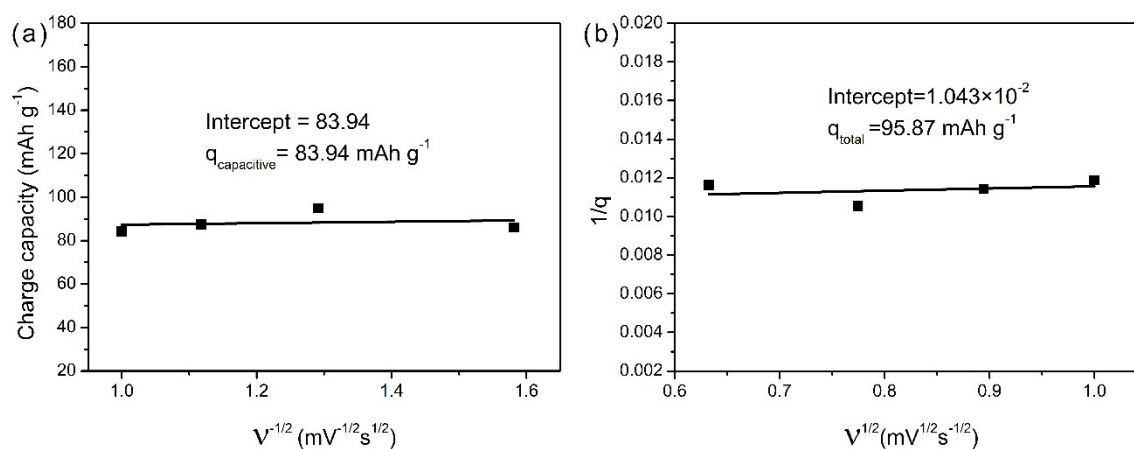


Figure S8. (a) The dependence of voltammetric charges versus $v^{-1/2}$. (b) The dependence of 1/total charge(q_{total}) versus $v^{1/2}$.

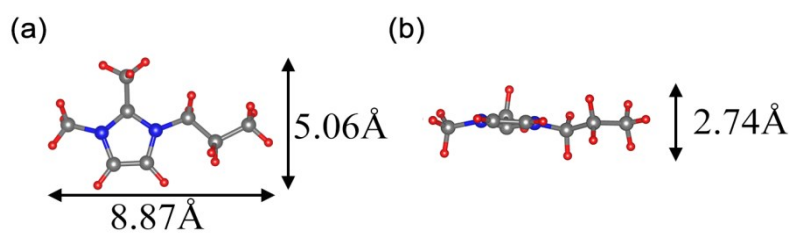


Figure S9. Optimized 1,2-dimethyl-3-propylimidazolium (DMPI) molecule using Vienna ab initio Simulation Package (VASP).

References

1. J. B. Cook, H.-S. Kim, Y. Yan, J. S. Ko, S. Robbennolt, B. Dunn and S. H. Tolbert, *Advanced Energy Materials*, 2016, **6**, 1501937.
2. S. Ardizzone, G. Fregonara and S. Trasatti, *Electrochim. Acta*, 1990, **35**, 263-267.
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