Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The Staging Mechanism of $AlCl_4$ Intercalation in Graphite Electrode for Aluminium-ion Battery

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Table S1: Geometrical parameters for the $AlCl_4$ intercalated structure at different sites; relative energy **(**ΔE) with respect to the B2 site, C-C bond lengths (d^{C-C}) and interlayer spacing between graphite layers.

Sites	**ΔE (eV)**	d^{C-C} **(Å)**	d **(Å)**
B1	0.009	1.423	8.639
B2	0.000	1.423	8.594
H	0.013	1.422	8.633
T	0.006	1.423	8.622

Figure S1: Schematic representation of the most stable B2 site.

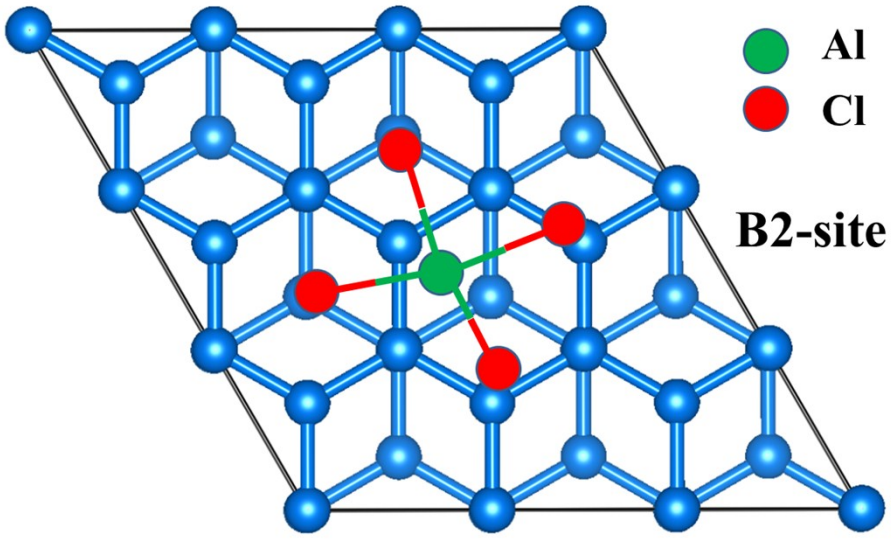

Figure S2: Molecular dynamics simulation analysis at different temperatures as a function of time step and the obtained structures, (a) 300K, (b) 400 K, (c) 500 K and (d) 600 K.

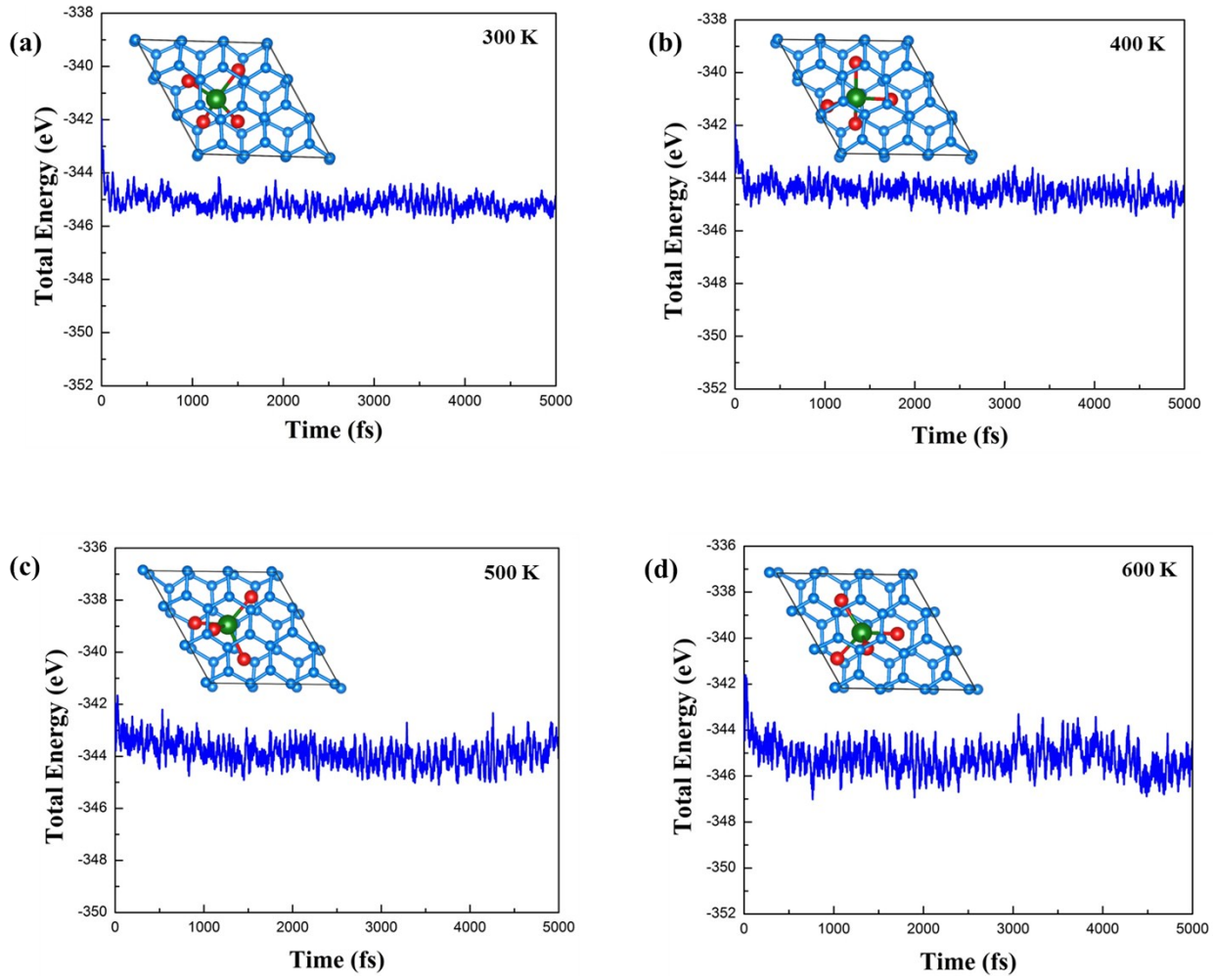

Figure S3: Side view of 6×6×2 supercell of graphite for stage-1, showing the arrangement of $AlCl_4$ ions in different stoichiometries considered: (a) $(AlCl_4)_4C_{288}$, (b) $(AlCl_4)_4C_{288}$, (c) $(AlCl_4)_4C_{288}$ and (d) $(AlCl_4)_4C_{288}$.

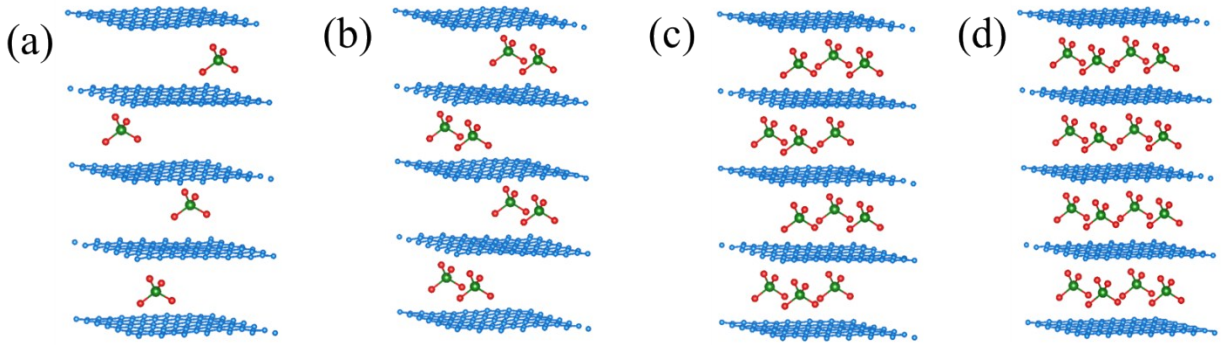

Figure S4: Side view of 6×6×2 supercell of graphite for stage-2, showing the arrangement of $AlCl_4$ ions in different stoichiometries considered: (a) $(AlCl_4)_2C_{288}$, (b) $(AlCl_4)_4C_{288}$, (c) $(AlCl_4)_6C_{288}$ and (d) $(AlCl_4)_8C_{288}$.

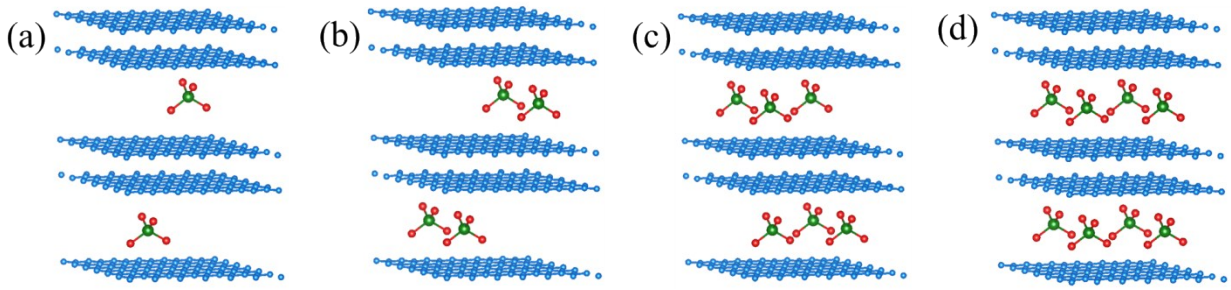

Figure S5: Side view of 6×6×3 supercell of graphite for stage-3, showing the arrangement of $AlCl_4$ ions in different stoichiometries considered: (a) $(AlCl_4)_2C_{432}$, (b) $(AlCl_4)_4C_{432}$, (c) $(AlCl_4)_6C_{432}$ and (d) $(AlCl_4)_8C_{432}$.

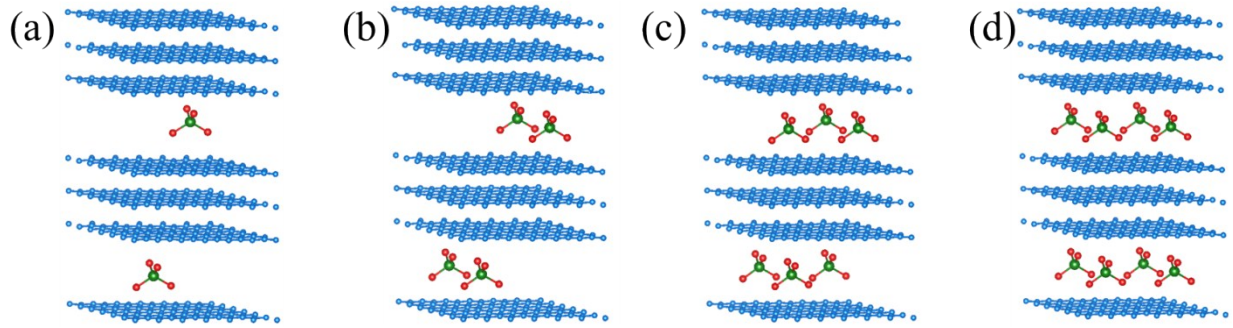

Figure S6: Side view of 6×6×2 supercell of graphite for stage-4, showing the arrangement of $AlCl_4$ ions in different stoichiometries considered: (a) $(AlCl_4)_1C_{288}$, (b) $(AlCl_4)_2C_{288}$, (c) $(AlCl_4)_3C_{288}$ and (d) $(AlCl_4)_4C_{288}$.

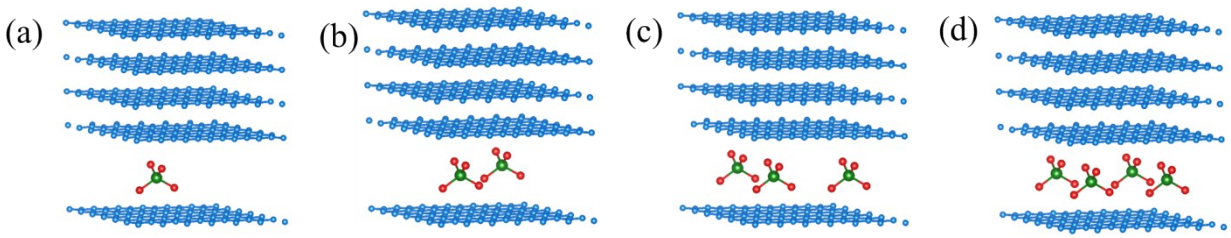

Figure S7: Binding energy per molecule for all stages of $AlCl_4$ as a function weight percentage of $AlCl_4$ in $(AlCl_4)_xC_{288}$.

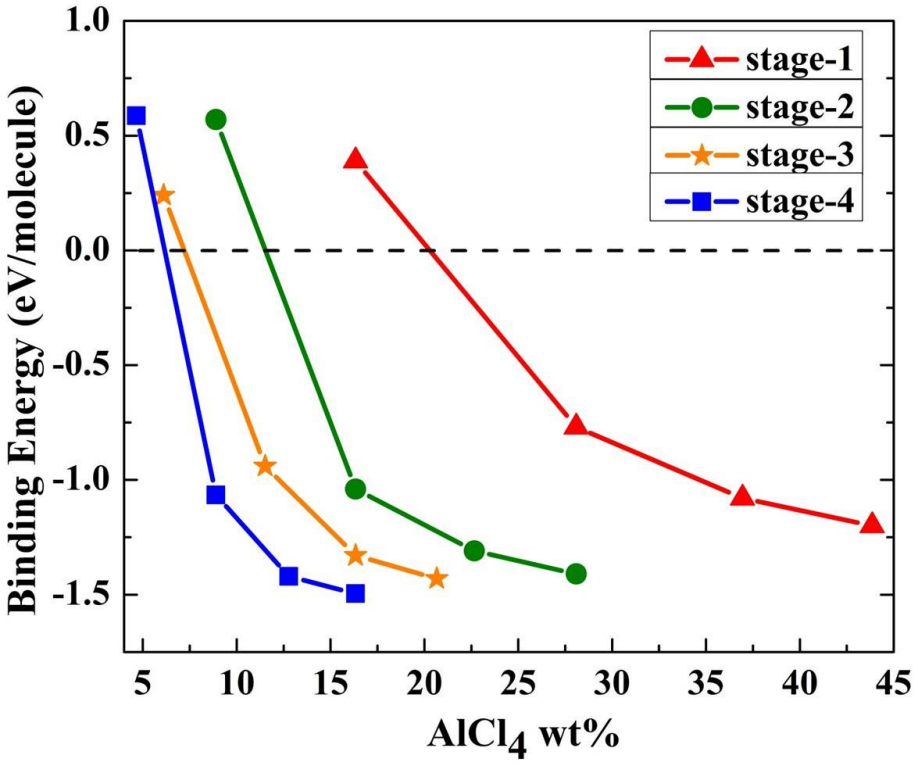

Table S2: Net effective charge calculated by Bader charge analysis.

Systems	**Bader Charge** |e|		
	Al	**Cl**	**Nearest C**
$AlCl_4$	+2.347	-0.587	
Graphite			+0.009
$AlCl_4$ intercalated graphite	+2.345	-0.801	+0.028