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Sphere-in-contact model for the development of new graphite-based intercalated battery materials

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We apply the sphere-in-contact model/theorem to the crystallographic analysis of graphite intercalation compounds (GICs), using a unit cell description based on the $A\alpha A\alpha$ stacking of two graphene layers. Under ambient conditions, the model predicts that LiC_6 has the largest diffusion rate parameter based on geometric considerations and repulsive interactions between intercalated atoms and has a thermodynamically stable lithium GIC stoichiometry; furthermore, two crystallographically distinct forms of LiC_8 are attainable but have lower diffusion rate parameters. Notably, the only experimental input required to predict stoichiometric stability is the interlayer spacing, which is readily obtained from X-ray diffraction (XRD) data. Additional empirical formulae— MC_2 , MC_3 , and M_3C_8 —are geometrically permissible but thermodynamically destabilised by repulsive interactions between intercalants. The density, packing fraction, and ion diffusivity during charge and discharge are derived analytically from the void space within the unit cell. The framework is broadly applicable to any intercalant and provides a simple, computationally and experimentally accessible basis for the rational design of graphite-based materials for next-generation ion-battery applications.

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1 Introduction

Li-ion batteries power smartphones, laptops, electric vehicles and other electronic devices that are now broadly used in many commercial applications.² Their invention is credited to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino, in 1979, with the Nobel Prize in Chemistry “for the development of lithium-ion batteries”.^{3–5} The battery anode in Li-ion batteries is composed of graphite, which stores the Li^+ cations during the charging cycle of the battery.⁶ The Li^+ cations diffuse between the basal planes of graphite, forming structures that resemble graphite intercalation compounds (GICs).⁷ The exact mechanism for the diffusion and storage of Li^+ cations in GICs is not well understood, and various mechanisms have been proposed to explain this phenomenon.⁸ In battery materials, the rate of charge–discharge cycles is a critical component in their design, and setups that require less time to be charged or discharged are being developed.⁹ This rate is associated with the rate of diffusion of Li^+ cations between the graphene layers of graphite.² Additionally, studies have investigated the electrochemical properties of graphite and alternative anode materials to improve rate capabilities, thermal stability, and overall energy density; a pursuit driven by the ever-rising demand for longer-lasting, higher-capacity batteries in consumer

electronics and electric vehicles.^{10,11} In this study, we have used sphere-in-contact models of GICs that have an $A\alpha A\alpha$ stacking sequence to study the diffusion of Li^+ cations within GICs with various empirical formulas. These empirical formulas were determined by the placement of the intercalated atoms on the basal plane of graphene in a configuration that minimizes the coulombic repulsive energy between cations. In general, these are intercalated structures that are hexagonally symmetric and place the intercalated atoms at their largest possible distances.

The sphere-in-contact model/theorem is a molecular and materials model where the atoms have their atomic radius (*e.g.* ionic radius, metallic and covalent). In this model, the spheres are in direct contact within structures held together by covalent, ionic or metallic bonding, and these structures show an improved representation of the electron cloud volume of an atom, an ion or even a metallic atom. We have previously shown that this model can better describe the structure of carbon materials (*e.g.* graphene, graphite, carbon nanotubes, fullerene) as it correctly shows the void space in the structure.¹² We have also used sphere-in-contact models to study the position of close-packed nanoparticles on metal surfaces¹³ and prepared miniature molecular models of heterogeneous catalysts, supported metal nanoparticles and organic molecules.¹⁴ We have also used the model for the elucidation of the cap structure of (3,3)-, (4,4)- and (5,5)-SWCNT, where physical sphere-in-contact models were constructed to understand the geometry of the spherical cap.¹⁵ As electromagnetic radiation interacts with the electron density cloud of atoms, the sphere-in-contact model was also applied to model the structure of an X-ray filter in

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which graphite had a rhombohedral structure.¹⁶ Recently, we have used such models to study diffusion mechanisms of adsorbates on close-packed metallic surfaces.¹⁷ So the use of the sphere-in-contact model is useful when analytical solutions of the distances between charged surfaces of atoms are desirable. These inter-surface distances can be used to evaluate the repulsive interaction energy between adsorbates and dopants in surface and materials chemistry using Coulomb's law, where the partial charges are not centred at the nucleus of the atoms, but rather on the surface of a sphere that has the atomic radius of the atom. The evaluation of Coulomb terms is computationally inexpensive and provides a method that can show clearly why certain symmetric dopant geometries or adsorbate structures are preferred, as they reduce the interatomic repulsive energy term. It is also useful as an educational tool as it directly translates concepts that students are taught in secondary school, such as basic laws of physics (*i.e.* Coulomb's law), mathematics (*e.g.* trigonometry and geometry) and the existence of partial charges in polar covalent bonds, to structures of doped materials and ordering of adsorbates on surfaces of metals and 2D layered materials (*e.g.* graphite intercalation compounds).

1.1 Computational studies of GICs as battery materials

Computational methods have been applied extensively in order to investigate the structural, energetic, and transport properties of graphite intercalation compounds (GICs), offering insights into lithium staging behaviour in layered materials such as graphite, interlayer interactions, and the dynamics of ion diffusion. Density functional theory (DFT) calculations that account for van der Waals interactions have demonstrated that the stability of lithium-intercalated graphite structures, such as LiC_6 and LiC_{12} configurations, sensitively depends on intercalant type, charge density, and interlayer spacing.^{18,19} These studies show that ionic size and the charge distribution of alkali metals influence both the spacing between graphite layers and the staging structure, which together impact lithium-ion (Li^+) mobility. Analysis of diffusion barriers has shown that lithium tends to move more easily along flat planes of graphite rather than between them, following paths that minimize repulsive interactions consistent with geometric models.²⁰ First-principles modelling of staged compounds has further helped to clarify how structural changes occur with shifts in ion concentration, emphasizing the energetic trade-offs between maintaining stage stability and transport efficiency.²¹ Molecular-scale simulations of graphite-electrolyte interfaces also suggest that solvent molecules and interfacial structure influence how easily ions move into the material and how likely the graphite layers respond and separate, with size and polarity effects closely linked to the spacing and arrangement of the graphite layers.^{22,23} These findings support the use of models that are more spatially focused such as the sphere-in-contact model, which helps visualize the space between atoms and offers an intuitive way to understand how 3D structure affects ion movement in such layered carbon materials.

1.2 Empirical formula of various GICs using the sphere-in-contact theorem

We have explored various possibilities for GICs using the sphere-in-contact theorem to model these materials. These models were designed on the assumption that intercalated atoms will have a partial positive charge due to charge transfer to the graphene layers. Therefore, these structures have configurations that maximise the distances of intercalants in order to reduce repulsive interactions and enhance the stability of the GIC. The partial charge sign in this treatment of repulsive intercalant interactions does not affect the energetic trends found for the various GICs as a function of intercalant concentration. With the use of this approach, we find some intercalation geometries that are depicted in Fig. 1, which show the position of the intercalants (red atoms) on the basal plane of graphene. The second graphene layer is omitted for clarity, but we assume an $\text{A}\alpha\text{A}\alpha$ stacking sequence of the graphene layers, which is known to be the stacking sequence in most GICs.¹

After exploring possible GICs, we find that the empirical formulas MC_2 , MC_6 , M_3C_8 , MC_3 and MC_8 are possible, although other less dense GICs are also feasible. The less dense GICs would not be of considerable interest, as the charge carrier density in such hypothetical GICs would not be high and such

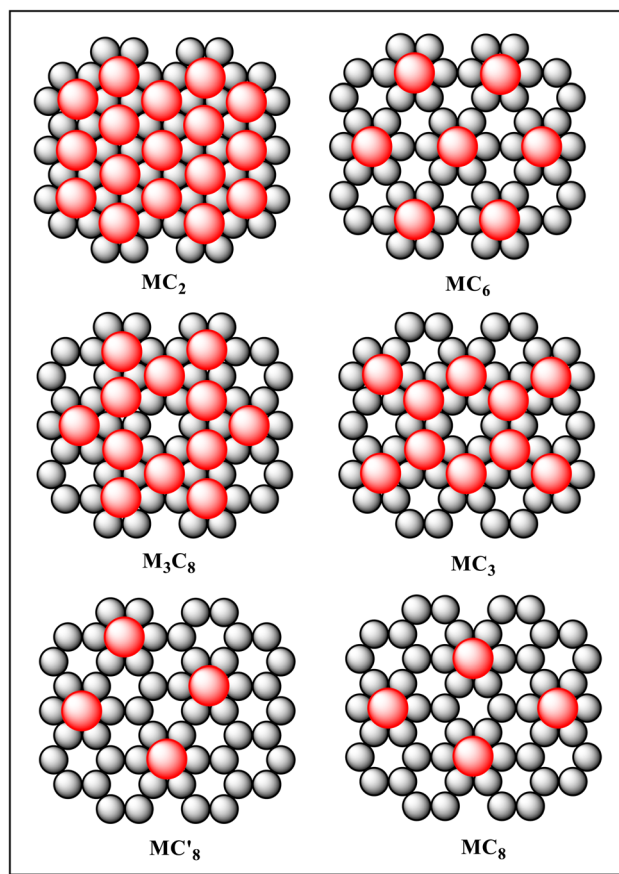


Fig. 1 Sphere-in-contact model of various graphite intercalation compounds (GICs). Red atoms are intercalants, and black atoms are carbon atoms. Pictures are drawn using ChemDraw.

materials would not have large charge capacities; therefore, their application in ion-battery materials would not be of practical use. Thus, we consider here only the aforementioned empirical formulas that are shown in Fig. 1.

1.3 Definition of unit cell in GICs

In this section, we define the unit cell of the various GICs shown in Fig. 1. On the basis of simple trigonometric and geometric rules, we can calculate the unit cell parameters in terms of three angles (*i.e.* α , β , and γ) and three unit cell vectors (*i.e.* a , b , and c). The angles of the lateral unit cell are depicted in Fig. 2, along with the various empirical formulas found.

In the calculations of the empirical formulas, we make use of the following basic geometric rules:

- (a) An atom at the corner of the unit cell will have 1/8 of its mass within the unit cell if the unit cell angles are all 90° .
- (b) An atom at the corner of a unit cell that has an angle ϕ and the other two 90° will have $\phi/720^\circ$ of its mass within the unit cell.
- (c) An atom at the edge of the unit cell will have $\frac{1}{4}$ of its mass within the unit cell if the unit cell angles are all 90° .
- (d) An atom at the edge of the unit cell where one of the angles is ϕ and the other two are 90° will have $\phi/360^\circ$ of its mass within the unit cell.

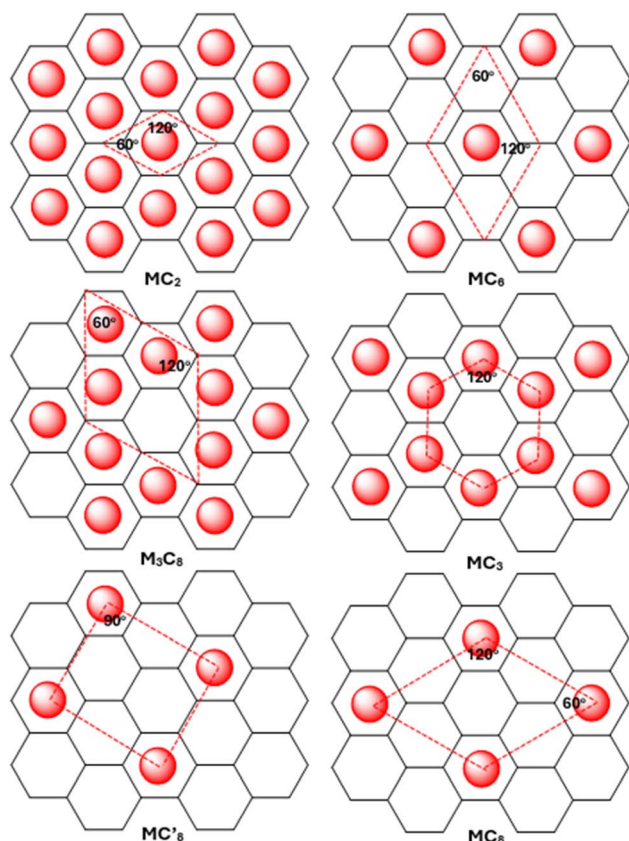


Fig. 2 Various sphere-in-contact models for GICs are shown, where the red atoms are intercalants and the hexagonal pattern is the graphene layer, showing the basal plane unit cell and angles. Pictures are drawn using ChemDraw.

(e) An atom at the side of the unit cell will have $\frac{1}{2}$ of its mass within the unit cell.

(f) An atom within the unit cell will have an equivalent of one atom in the unit cell.

Using these rules, we derive the various empirical formulas shown in Fig. 2, with the assumption that the intercalants will always reside in the center of the hexagonal ring on the graphene layers, due to the higher coordination number at these positions, which reduces the charge on the intercalant and therefore the GIC would be more stable. Also, the configuration of intercalants is such that there is a maximum average distance between them, which would minimise the repulsive energy between the intercalants and therefore would be a lower-energy configuration. This would also presumably be a preferred configuration when the ion-battery material is not in a charged state.

1.4 Calculation of the density of various GICs within the sphere-in-contact model

The density of an arbitrary GIC using the sphere-in-contact model can be defined as

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{(N_{\text{Li}} \times m_{\text{Li}}) + (N_{\text{C}} \times m_{\text{C}})}{V_{\text{unit cell}}} \quad (1)$$

The volume of any unit cell in a material can be calculated from the volume of the triclinic unit system, which is given by

$$V_{\text{unit cell}} = a \times b \times c \times \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \times \cos \alpha \times \cos \beta \times \cos \gamma} \quad (2)$$

where a , b and c are the lattice vectors and α , β and γ are the angles between the lattice vectors, as shown in Fig. 3.

Here, the primitive unit cell has a rhombus base and height c . If we start from the volume of the triclinic unit cell, the unit cell volume is given by,

$$V_{\text{unit cell}} = a^2 \times c \times \sin \gamma \quad (3)$$

where $a = 2 \times \sqrt{3} \times r_{\text{C}}$ and $\gamma = 60^\circ$ and c is the height of the unit cell of the GIC, which is given by,

$$c = 2 \times \sqrt{(r_{\text{C}} + r_{\text{Li}})^2 - 4 \times r_{\text{C}}^2} \quad (4)$$

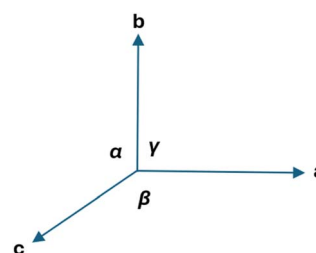


Fig. 3 Figure showing the lattice vectors and angles in the hexagonal unit cell.

The trigonometric and geometric derivation of the height of the unit cell is given in Section 1.5.

The density of the GIC is obtained by combining eqn (1), (3) and (4) and is given by

$$\rho(\text{GIC}) = \frac{(N_{\text{Li}} \times m_{\text{Li}}) + (N_{\text{C}} \times m_{\text{C}})}{2 \times a^2 \times \sin \gamma \sqrt{(r_{\text{C}} + r_{\text{Li}})^2 - 4 \times r_{\text{C}}^2}} \quad (5)$$

where N_{Li} and N_{C} are the number of lithium and carbon atoms within the unit cell of the GIC, respectively, m_{Li} and m_{C} are the atomic masses of Li and C, respectively, and r_{Li} and r_{C} are the atomic radii of the lithium ion and the covalent radius of carbon in graphite, respectively. Notably, this equation is not limited to Li-ion GICs but can be used for any monoatomic (e.g. Li, Na, K, Rb, Cs) intercalants between graphite layers.

We have used the cationic radius of lithium to calculate whether the densities of such GICs depend on the charged state of the GIC. In the presence of an external electric field that is parallel to the graphite basal plane, we expect that the mobile intercalant species are cationic lithium atoms, mainly due to their smaller radius and charge compared to the atomic radius of a neutral lithium atom. It is also conceivable that not all intercalants are in the same charged state during the charging/discharging of such materials. So, the radius of the intercalant can be between the atomic and ionic radii of lithium, and the charged state of the intercalated atoms mainly affects the interlayer distance. The carbon hexagonal framework is affected to a smaller extent, as the interatomic distances are mainly determined by the σ covalent framework, which does not participate in the bonding with the intercalants. Based on MP2 calculations of the lithium cation between two benzene rings, we observe little variation in the C–C bond lengths, which are not affected by the formation of the ion– π bond between lithium cations and the conjugated π -clouds in cyclic carbon rings.

1.5 Height of the unit cell using the sphere-in-contact model for lithium GICs

Fig. 4 shows the top and side views of an arbitrary GIC with an $A\alpha A\alpha$ stacking sequence, where the intercalants are in the center of the hexagonal ring of graphite and in which the height of the unit cell is shown (c). By applying Pythagoras' theorem and the dimensions of the triangle shown in Fig. 4, given as a function of the radius of the carbon atom and the radius of a lithium cation, we are able to calculate the height of the unit cell, which is given by c . We only consider GIC models where the interlayer spacing between the graphene layers is that of LiC_6 , which has been found to be a stable form of lithium graphite intercalation compounds under ambient pressure and temperature conditions. We expect this assumption to be valid if the intercalation of lithium atoms is maximum when there is one lithium atom per hexagonal ring of graphite and every layer of graphite is fully saturated with lithium atoms; moreover, it has been previously confirmed *via in situ* neutron diffraction that the lattice dilation during charging of lithium ion batteries is only 4%,²⁴ which corresponds to an empirical formula of LiC_6 . However, in this study, we explore some higher Li^+

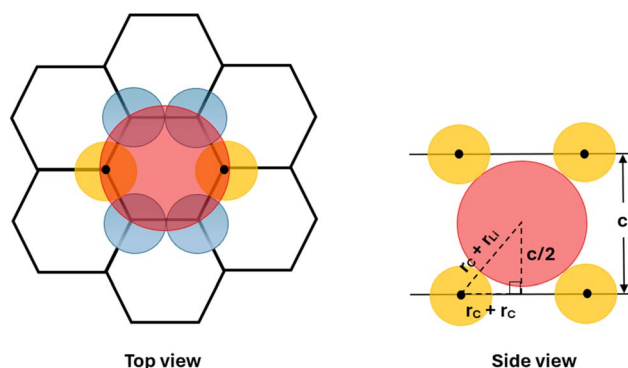


Fig. 4 Top and side view of the trigonometric and geometric derivation of the height of the unit cell (c) in the GIC using the sphere-in-contact model. Lithium atoms are shown in red, and carbon atoms are shown in blue and orange. The carbon atom centers are indicated with black dots.

concentration phases in GICs as we expect, based purely on geometric considerations, that such higher lithium density phases in graphite would also result in lattice dilation of the order of 4%. This is based on a number of experimental and computational studies that suggest that such superdense lithium phases are possible for an empirical formula of LiC_2 , which is the highest density phase considered in this study. For example, XPS studies with the use of a piston-cylinder high-pressure chamber indicate that lithium intercalation to LiC_2 causes insignificant changes in the chemical shifts of carbon atoms, consistent with the assumption made here that there is not a significant lattice dilation when the LiC_6 and LiC_2 structures are compared.²⁵ Lithium over-intercalation, beyond LiC_6 , has also been observed recently at ambient pressure, using static ^7Li nuclear magnetic resonance (NMR), although this has been found to be a minor component in the predominantly LiC_6 structure.²⁶ A very recent study that used ball milling to prepare LiC_3 under ambient conditions found that this structure is also stable under ambient conditions.²⁷ Notably, the stability of the LiC_3 phase was previously predicted on the basis of density functional theory (DFT) calculations, in addition to the existence of a LiC_2 phase, which was found to be metastable.²⁸

We therefore assume that one Li^+ per carbon ring is the maximum Li ion concentration that can be evaluated using the current approach within the sphere-in-contact model, and that the interlayer distance is the same for highly dense Li-ion GICs because the dense LiC_2 phase would result in a possible error of less than 4% in the volume calculation of the unit cell, compared to other arbitrary GICs. We note here that although we explore these high-density phases of lithium in graphite, such as LiC_3 and LiC_2 , such high-density phases could result in considerable clustering between lithium ions into metallic lithium clusters, under reducing conditions. Such metallic clusters for lithium have been observed *via* infrared spectroscopy of LiC_4 and LiC_2 (ref. 29) and are potential pathways for the chemical and mechanical degradation of such lithium ion GICs, in ion-battery materials, under reducing conditions (*i.e.* an excess of electrons within these materials).

1.6 Interlayer distance in LiC₆ and radius of intercalated Li atoms

There have been many crystallographic studies to accurately estimate the interlayer spacing in LiC₆ and the stacking sequence. Crystallography suggests that the stacking sequence is *AzAz*, with an interlayer distance of 3.70 Å, based on the stable form of this GIC at ambient temperature and pressure, in samples that were prepared by annealing or under pressure, causing lithium to intercalate between the layers.¹ This interlayer distance is also in agreement with a study that investigated the distance as a function of lithium intercalation, obtaining the phase diagram of Li_xC₆, where *x* was varied between 0 and 1.³⁰ Additionally, LiC₆ prepared by electrochemical reduction of natural graphite in a LiClO₄ solution at 30 °C exhibited an interlayer distance of 3.70 Å.³¹ This interlayer distance of 3.70 Å, as well as the *AzAz* stacking sequence, was also confirmed by neutron diffraction at various temperatures.³² This interlayer distance is increased by 10.3% compared to that of hexagonal ABAB stacked graphite (3.354 Å)³³ due to Li intercalation. We have therefore used this distance to estimate the radius of lithium ions within the sphere-in-contact model, when the carbon atoms have a covalent radius that corresponds to half a bond length of the C–C bond in graphite (1.422 Å).³³ With the use of Fig. 4, we therefore calculated the radius of the lithium ions in the sphere-in-contact model to be 1.62 Å and the covalent radius of carbon to be 0.711 Å.

In the next section, we show the calculations of the unit cell volume and the density in GICs using eqn (5) and the radius of intercalated lithium atoms, $r_{\text{Li}} = 1.62 \times 10^{-8}$ cm, and the covalent radius for carbon $r_{\text{C}} = 0.711 \times 10^{-8}$ cm.

1.7 Density and volume of the unit cell of GIC

The volume of the unit cell of LiC₆ is,

$$V_{\text{LiC}_6} = 36\sqrt{3}r_{\text{C}}^2\sqrt{(r_{\text{C}} + r_{\text{Li}})^2 - 4 \times r_{\text{C}}^2} = 5.822 \times 10^{-23} \text{ cm}^3 \quad (6)$$

The GIC with the empirical formula LiC₆ has one Li atom and six carbon atoms per unit cell, so the density is given by

$$\rho = \frac{m_{\text{Li}} + 6 \times m_{\text{C}}}{V_{\text{LiC}_6}} \quad (7)$$

where m_{Li} and m_{C} are the masses of the lithium and carbon atoms, which were calculated from the atomic masses of these atoms as taken from the IUPAC periodic table and are $m_{\text{Li}} = 1.1526 \times 10^{-23}$ g and $m_{\text{C}} = 1.9944 \times 10^{-23}$ g. So the density of LiC₆ is 2.25 g cm⁻³, which is in excellent agreement with the literature value of 2.21 g cm⁻³ based on XRD.¹ This suggests that Li in LiC₆ is in a +1 charged state under ambient conditions, but, due to the soft repulsive wall of the carbon π -cloud, its radius is closer to the atomic (*i.e.* the 12-coordinated metallic radius) radius of Li (1.5 Å),³⁴ rather than the ionic radius of Li⁺ ($r_{\text{CN}_4} = 0.59$ Å, $r_{\text{CN}_6} = 0.76$ Å, $r_{\text{CN}_8} = 0.92$ Å)³⁵ estimated from empirical analysis of interatomic distances in lithium oxides. This is also in good agreement with Bader AIM calculations in the 4-layer model of LiC₆, which estimates a charge of +0.88 on

lithium.³⁶ This is an interesting result that is mainly associated with the property of lithium having a significantly larger radius than carbon, which is associated with the smaller effective nuclear charge of lithium (Z_{eff}) compared to carbon. Furthermore, it suggests that, based on the atom radius of Li in the sphere-in-contact model, the densest phase of lithium in graphite is LiC₆. Any further addition of Li to graphite, forming LiC₂ and LiC₃, which have been suggested as superdense phases of lithium atoms in GICs, would result in a significant overlap of the electron densities of the lithium atoms, which would suggest a rather metallic 2D array of lithium atoms, rather than isolated lithium atoms. This is perhaps the reason that these superdense configurations of lithium atoms in GICs are not observed under ambient conditions and require mechanical compression or other extreme electrochemical conditions.

In Table 1, we present the calculated volume of the unit cell in the various empirical formulas studied, and in Table 2 we present the density along with analytical equations to calculate this based on the sphere-in-contact model of LiC₆.

These densities were compared to crystallographically determined densities and are in excellent agreement, although the stacking sequences of these GICs differ from the *AzAz* stacking found in LiC₆. This indicates that the intercalant concentration calculated for the various empirical formulas can be used to estimate the ion diffusion rates and conductivities in an electric field without significant error (Table 3).

We calculate an average percent error for using the sphere-in-contact method to model the structure and density of GICs to be 1.59%, which is comparable to the 1–2% error known for commonly used XC correlation functionals in DFT, such as PBE-D3 and PBEsol.

1.8 Packing fraction of GICs and diffusion rate of intercalants

From the packing fraction, the available space for intercalant diffusion can be estimated. The void space fraction of the atoms in a unit cell is given as 1 minus the packing fraction. Therefore, the void space in a material correlates to the space available for atom/ion (*i.e.* intercalant) diffusion. This correlation can be made based on the fact that the lowest barrier for intercalant diffusion within the graphene sheets will be roughly the same for any density of intercalants between the layers, as intercalants are held by weaker interactions (*e.g.* ion– π interactions), compared to the stronger covalent C–C bonds within the graphene layers. This barrier is expected to be lower over the C–C bonds of the graphene layers, rather than over the C positions, as the coordination is greater when the adsorbate is directly on top of the covalent bonds connecting the carbon atoms, which suggests a lower barrier for diffusion from the center of one hexagonal carbon ring to the centre of an adjacent hexagonal ring (see Fig. 2). So the parameter that limits the diffusion in the case of GICs is not the barrier for diffusion but the available void space between the layers and the path that the ions follow during this diffusion, which also determines the capacity of the batteries. This is based on a physical understanding of this material, which suggests that the barrier to diffusion is very

Table 1 Unit cell volume of the various empirical formulas of GICs using the sphere-in-contact model

Formula	Analytical equation of density	$V_{\text{Li, GIC}} (10^{-23} \text{ cm}^3)$	$V_{\text{Na, GIC}} (10^{-23} \text{ cm}^3)$	$V_{\text{K, GIC}} (10^{-23} \text{ cm}^3)$	$V_{\text{Rb, GIC}} (10^{-23} \text{ cm}^3)$	$V_{\text{Cs, GIC}} (10^{-23} \text{ cm}^3)$
MC ₂	$12\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}$	1.94	2.17	2.79	2.91	3.26
MC ₆	$36\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}$	5.82	6.52	8.37	8.72	9.77
M ₃ C ₈	$48\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}$	7.76	8.70	11.15	11.63	13.03
MC ₃	$36\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}$	5.82	6.52	8.37	8.72	9.77
MC ₈ '	$48\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}$	7.76	8.70	11.15	11.63	13.03
MC ₈	$48\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}$	7.76	8.70	11.15	11.63	13.03

Table 2 Empirical formulas and densities using the sphere-in-contact model for various group 1 (i.e., Li, Na, K, Rb, and Cs) intercalated GICs

Formula	Analytical equation of density	$\rho_{\text{Li, GIC}} (\text{g cm}^{-3})$	$\rho_{\text{Na, GIC}} (\text{g cm}^{-3})$	$\rho_{\text{K, GIC}} (\text{g cm}^{-3})$	$\rho_{\text{Rb, GIC}} (\text{g cm}^{-3})$	$\rho_{\text{Cs, GIC}} (\text{g cm}^{-3})$
MC ₂	$\frac{m_{\text{M}} + 2 \times m_{\text{C}}}{12\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}$	2.65	3.59	3.76	6.25	8.00
MC ₆	$\frac{m_{\text{M}} + 6 \times m_{\text{C}}}{36\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}$	2.25	2.42	2.21	3.00	3.48
M ₃ C ₈	$\frac{3 \times m_{\text{M}} + 8 \times m_{\text{C}}}{48\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}$	2.50	3.15	3.18	5.03	6.31
MC ₃	$\frac{2 \times m_{\text{M}} + 6 \times m_{\text{C}}}{36\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}$	2.45	3.00	2.98	4.63	5.74
MC ₈ '	$\frac{m_{\text{M}} + 8 \times m_{\text{C}}}{48\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}$	2.20	2.27	2.01	2.59	2.92
MC ₈	$\frac{m_{\text{M}} + 8 \times m_{\text{C}}}{48\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}$	2.20	2.27	2.01	2.59	2.92

Table 3 Comparison of densities calculated using the sphere-in-contact model and XRD-determined densities of MC₈, where M = K, Rb, and Cs

GIC empirical formula	Density (this study) (g cm ⁻³)	Density XRD (g cm ⁻³)	Ref.
KC ₈	2.01	2.00	1
RbC ₈	2.59	2.55	37
CsC ₈	2.92	3.00	38

high if there is already an intercalant in the adjacent hexagonal ring. We therefore suggest that the packing fraction using the sphere-in-contact model can be used in materials design as an efficient method to screen the ion conductivities of various GIC libraries.

Although there are no reported crystallographic structures for LiC₁₀, there have been reports of GICs with empirical formula MC₈. KC₈, RbC₈, and CsC₈ are known examples of GICs with this empirical formula,³⁹ which is a less dense phase of the intercalated atoms in graphite. This is perhaps associated with the atomic radius of the intercalant potassium ($r_{\text{K}} = 2.3 \text{ \AA}$),³⁴ rubidium ($r_{\text{Rb}} = 2.5 \text{ \AA}$)³⁴ and caesium ($r_{\text{Cs}} = 2.7 \text{ \AA}$),³⁴ which all have significantly larger radii than Li ($r_{\text{Li}} = 1.5 \text{ \AA}$)³⁴ and are therefore more stable at a larger separation, preventing their

transition to a 2D metallic state. This is in agreement with the interatomic distance of intercalants in the MC₈ empirical formula, in which the interatomic distance between intercalants is about 4.926 Å, and consequently the nearest surface-to-surface distance between intercalants is larger than the interatomic distance between intercalants in the MC₆ structure, which is about 4.266 Å. Therefore, the MC₈ structure in the sphere-in-contact model will have smaller repulsion between the intercalated atoms, and, therefore, bulkier atoms can be accommodated between the layers, at larger separations. The effect of the radius of these atoms on the interlayer distance in MC₈ for potassium ($d_{\text{K}} = 5.35 \text{ \AA}$),³⁷ rubidium ($d_{\text{Rb}} = 5.65 \text{ \AA}$)³⁷ and cesium ($d_{\text{Cs}} = 5.94 \text{ \AA}$) has been previously reported and is consistent with the trend of their atomic radii.³⁷

Additionally, it is possible that an MC₈' structure can exist, as based on the interatomic distances between intercalants it would have intermediate stability to that of LiC₆ and LiC₈. However, in this structure the interatomic distances in one direction are different from those in the perpendicular direction, so 2D anisotropy would be expected, and this structure would be more stable if it relaxes to MC₈, based on the repulsive interactions between intercalants, as presented in Section 1.9.

From the packing fraction, the available space for intercalant diffusion can be estimated. The packing fraction is the % space

occupied by the atoms in the unit cell of the material. Therefore, the packing fraction is inversely proportional to the available empty space (*i.e.* void space) in a material, which correlates to the space available for atom/ion (*i.e.* intercalant) diffusion. This correlation can be made based on evidence that the lowest barrier for intercalant diffusion within the graphene sheets will be roughly the same for any density of intercalants between the layers as intercalants are held by weaker interactions (*e.g.* ion- π interactions), compared to the stronger covalent C-C bonds within the graphene layers. This barrier is expected to be lower over the C-C bonds of the graphene layer rather than over the C positions, as the coordination is greater when the adsorbate is directly on top of the covalent bonds connecting the carbon atoms, which suggests a lower barrier for diffusion from the center of one hexagonal carbon ring to the centre of an adjacent hexagonal ring. The barrier for this diffusion has been previously estimated based on DFT calculations, and it was found that, for larger interlayer spacing, this barrier reduces, increasing therefore the diffusion rate by 3 orders of magnitude when the interlayer distance increases from 3.4 to 3.8 Å.⁴⁰ In addition to this, it is conceivable that when the intercalants are in close proximity, the barrier for ion diffusion will become exponentially high due to overlap of their electron density clouds, increasing the repulsive interactions considerably. So this suggests that a more important factor for the diffusion of intercalants between graphite layers is the available void space, which is inversely proportional to the atomic packing fraction (η) given by

$$\eta = \frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}} \quad (8)$$

So we can approximate the diffusion rate parameter (D) as being proportional to the void space given by

$$D \propto 1 - \eta \quad (9)$$

Apart from this purely geometric factor, the relative charge transfer rate is directly proportional to the molar intercalant density C (units: $\text{mol} \cdot \text{cm}^{-3}$) of the GIC, which is given by the number of intercalant atoms in the unit cell divided by the volume of the unit cell and Avogadro's number

$$D \propto C = \frac{\text{number of intercalate atoms in unit cell}}{N_{\text{Av}} \times V_{\text{unit cell}}} \quad (10)$$

So the intercalant diffusion rate parameter is proportional to

$$D \propto C \times (1 - \eta) \quad (11)$$

As the specific atomic radius of the intercalated atoms, for certain empirical formulas, results in considerable overlap of the electron cloud of the intercalated atoms, the void space in the sphere-in-contact model can also obtain negative values when the intercalant density is very high (*e.g.* MC_2). These structures have not been considered in the trends of intercalant diffusion rate. In this analysis, we only consider the structures where the intercalated atoms do not overlap based on their

atomic radius, which were found to be the empirical formulas MC_6 , MC'_8 and MC_8 , as the nearest neighbour interatomic intercalant distances were 4.266 Å, 4.524 Å and 4.524 Å, respectively. These interatomic distances are larger than two times the atomic radius of the corresponding intercalants, which are 2.9 Å, 3.6 Å, 4.4 Å, 4.7 Å and 5.4 Å for Li, Na, K, Rb and Cs, respectively.⁴¹ Here, we find that for the other structures (MC_2 , M_3C_8 and MC_3) the nearest neighbour intercalant distance is only 2.463 Å, which is less than two times the atomic radius of any of the group 1 intercalants.⁴¹ Such structures would result in a 2D metallic state of the intercalated atoms, and would render the material unsuitable for graphite-based battery applications. Based on this analysis, we find that the trends in intercalant diffusion rates for the various group 1 elements with the MC_6 empirical formula are

$$\text{LiC}_6 = 0.0154 > \text{NaC}_6 = 0.0124 > \text{KC}_6 = 0.0056 > \text{RbC}_6 = 0.0044 > \text{CsC}_6 = 0.0011$$

This trend suggests that intercalated lithium is the GIC that would have the largest diffusion rate of intercalated atoms, but, interestingly, a NaC_6 GIC would only be 20% less efficient, based on geometric considerations. Here, we note that, in practise, a stable phase of NaC_6 does not exist, but it has been prepared under high pressures. The sphere-in-contact model also suggests that, based on the overlap of intercalated atoms, KC_6 , RbC_6 and CsC_6 are not stable under ambient pressure and temperature. So, we provide here a computationally very efficient way to screen various GICs for their efficiency as ion-battery materials using as input only the atomic radii of atoms in the GIC and using the sphere-in-contact model. For the empirical formulas of GICs considered, we provide the value of the packing fraction in Table 4, which can be used to screen the diffusion rate parameters of any GIC with $A\alpha A\alpha$ stacking (shown in Table 5), given only the radii of the intercalants and carbon atoms. Based on the results shown in Table 5, we find using the sphere-in-contact model that LiC_6 would have the highest ion conductivity in its use as a battery material, which is in agreement with the structure of LiC_6 in its fully charged state.^{1,30,31,42} It is noted that, although the staging in ion-graphite materials studied here is not explicitly considered in estimating the trends of ion diffusion, most of the ion diffusivity is due to intralayer diffusion rather than interlayer diffusion. This suggests that the model employed can be used for screening various ion-graphite-based materials, but the exact calculation of the diffusion rate would require more advanced computer models. This could, in principle, be performed with a computer code that treats the partial charges of the lithium ions as being at the contact points with the surrounding C atoms for each lithium ion intercalant. This would form charge-transfer-induced dipole moments along the C-Li bonds, and the electric field from these dipoles could have an effect on the staging of ions and their diffusion across graphitic islands within a graphite model that includes grain boundaries and other defects.

Table 4 Packing fraction (η) of the various empirical formulas of GICs using the sphere-in-contact model. The radii used for Li, Na, K, Rb and Cs are 1.62 Å, 1.8 Å, 2.3 Å, 2.4 Å and 2.7 Å, respectively

Formula	Analytical equation of density	$\eta_{\text{Li, GIC}}$	$\eta_{\text{Na, GIC}}$	$\eta_{\text{K, GIC}}$	$\eta_{\text{Rb, GIC}}$	$\eta_{\text{Cs, GIC}}$
MC ₂	$\frac{4}{3} \times \pi \times r_{\text{M}}^3 + \frac{8}{3} \times \pi \times r_{\text{C}}^3$	1.073	1.262	1.936	2.095	2.623
MC ₆	$\frac{12\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}{\frac{4}{3} \times \pi \times r_{\text{M}}^3 + \frac{24}{3} \times \pi \times r_{\text{C}}^3}$	0.461	0.513	0.717	0.767	0.936
M ₃ C ₈	$\frac{36\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}{4 \times \pi \times r_{\text{M}}^3 + \frac{32}{3} \times \pi \times r_{\text{C}}^3}$	0.843	0.981	1.479	2.130	1.991
MC ₃	$\frac{48\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}{\frac{8}{3} \times \pi \times r_{\text{M}}^3 + \frac{24}{3} \times \pi \times r_{\text{C}}^3}$	0.383	0.444	0.663	0.716	0.890
MC ₈ '	$\frac{36\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}{\frac{4}{3} \times \pi \times r_{\text{M}}^3 + \frac{32}{3} \times \pi \times r_{\text{C}}^3}$	0.385	0.419	0.565	0.602	0.725
MC ₈	$\frac{48\sqrt{3} \times r_{\text{C}}^2 \sqrt{(r_{\text{C}} + r_{\text{M}})^2 - 4 \times r_{\text{C}}^2}}{\frac{4}{3} \times \pi \times r_{\text{M}}^3 + \frac{32}{3} \times \pi \times r_{\text{C}}^3}$	0.385	0.419	0.565	0.602	0.725

Table 5 Diffusion rate parameter (descriptor D) of intercalants with various empirical GIC formulas using the sphere-in-contact model

Formula	Minimum intercalant distance	$D_{\text{Li, GIC}} (\text{g cm}^{-3})$	$D_{\text{Na, GIC}} (\text{g cm}^{-3})$	$D_{\text{K, GIC}} (\text{g cm}^{-3})$	$D_{\text{Rb, GIC}} (\text{g cm}^{-3})$	$D_{\text{Cs, GIC}} (\text{g cm}^{-3})$
MC ₂	$2\sqrt{3}r_{\text{C}} = 2.463 \text{ Å}$	−0.0062	−0.0200	−0.0557	−0.0626	−0.0827
MC ₆	$6 \times r_{\text{C}} = 4.266 \text{ Å}$	0.0154^a	0.0124	0.0056	0.0044	0.0011
M ₃ C ₈	$2\sqrt{3}r_{\text{C}} = 2.463 \text{ Å}$	0.0100	0.0011	−0.0214	−0.0484	−0.0379
MC ₃	$2\sqrt{3}r_{\text{C}} = 2.463 \text{ Å}$	0.0352	0.0283	0.0134	0.0108	0.0037
MC ₈ '	$6 \times r_{\text{C}} = 4.266 \text{ Å}$	0.0132	0.0111	0.0065	0.0057	0.0035
MC ₈	$4\sqrt{3}r_{\text{C}} = 4.927 \text{ Å}$	0.0132	0.0111	0.0065	0.0057	0.0035

^a Bold values of diffusion rates indicate structures without overlapping intercalants; these are stable structures. Negative values indicate structures without any void space for intercalant diffusion. LiC₆ that has the highest diffusion rate parameter, as shown in red.

1.9 Calculation of the interatomic repulsive energy (U_{net}) between intercalants to assess the stability of an arbitrary GIC

To calculate the interactions between intercalants, we have used a supercell approach for the various GICs in Fig. 1, as shown in Fig. 5. We also assumed that the interactions between intercalants are up to the 8th nearest neighbour, which is about 8 Å, depending on the atomic radius of the intercalant. This assumption is valid as the partial charges on the surfaces of the atoms are significantly screened by the electron clouds of nearby intercalated atoms. We have counted all 8 nearest neighbour interactions (*i.e.* d_i , where $i = 1, 2, 3, 4, 5, 6, 7, 8$) of the various configurations shown in Fig. 5, as shown in Table 1. We then used the following trigonometric and geometric derivations to calculate the repulsive interactions between partial point charges at the nearest distance between the intercalated spheres. A similar equation was used to calculate the repulsive

interaction between adsorbates on HCP and FCC metal surfaces.¹⁷ This equation is a summation of all the pairwise interactions, up to the 8th nearest neighbour intercalants. We assume that the partial charge on the surface of the intercalant is constant and does not depend on the interactions between the intercalant (which would generate a local electric field), but only depends on the coordination number (CN) that the intercalant has with the graphene layer (*i.e.* the contact points of the intercalated sphere with the carbon atoms). Since the intercalants in all the GICs in this study reside at the middle of the hexagon in each carbon ring, and the stacking of the layers is $A\alpha A\alpha$, we can calculate the repulsive energy between intercalants in these GIC models, depending on the saturation with lithium ions, during charging and discharging of the battery material. The coordination number of the intercalant is 12, as there are 6 carbon atoms in the first layer and 6 carbon atoms in the second layer that are in direct contact with the intercalant.

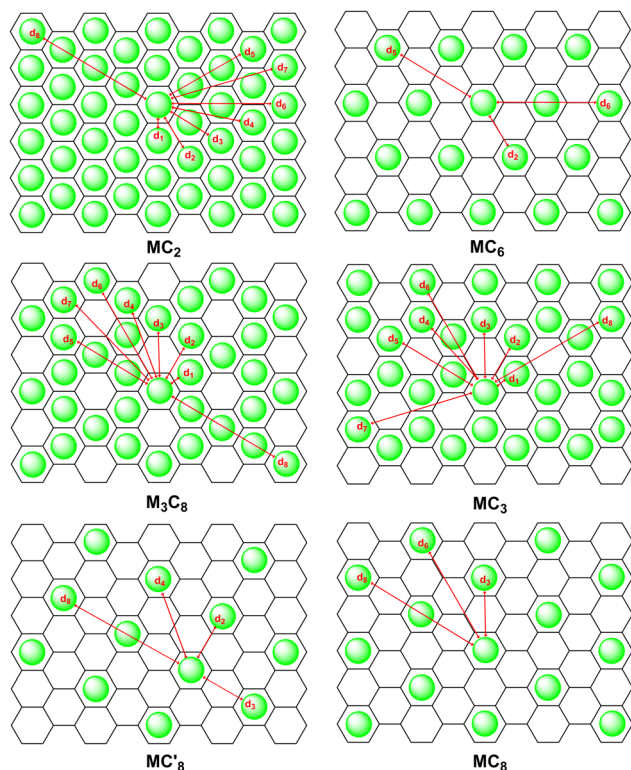


Fig. 5 Nearest neighbour interactions between intercalants (green) in various GICs. The graphene layer is shown by a hexagonal wire-frame model.

As lithium is a group 1 element and it tends to lose one electron to become more stable, the charge on each lithium will be +1. But since some of this electronic charge of the ionised electron is transferred to the carbon rings in direct contact with the intercalant, which then forms a π -ion bond, the partial charge on the intercalant will only be a fraction of +1. We can estimate that it will be $+1/12e$ because the coordination number of the intercalant is 12. Here, we note that the absolute value of the partial charge on the intercalate surface is not a critical parameter in the sphere-in-contact model of GICs, in order to obtain trends of repulsive energy between intercalants (this will be shown later). So we used a partial charge of $+0.08e$ and $+0.16e$ (this is a positive partial charge) to give us an indication of the repulsive interaction energy trends between intercalants in the various GICs, and whether this affects the calculated trends. We observe that the absolute value of the partial charge used does

not affect the trends in the repulsive energy between intercalants (see Table 6). Therefore, this approach can be applied to understand the relative stability of the various GIC phases found.

Furthermore, we provide a trigonometric equation that quantifies the stability of the various GICs and can be used to assess the internal energy (U_{net}) associated with various GICs, in a charged state, by changing the partial charge on the intercalants. This equation has as dependent variables the atomic radius of the carbon atom (r_C) and the intercalant (r_M) and the partial charge on the intercalate surface (δ); these are $r_C = 0.709 \times 10^{-8}$ cm and $r_{\text{Li}} = 1.52 \times 10^{-8}$ cm, respectively, for Li_xC_y GICs. These trigonometric equations are shown next.

The distances between the intercalants are given by the following trigonometric equations. These are functions of the atomic radius of the carbon atom and the atomic radius of the intercalant. So they can be applied to any GIC and are,

$$d_1 = 2(\sqrt{3}r_C - r_M) \quad (12)$$

$$d_2 = 2(3r_C - r_M) \quad (13)$$

$$d_3 = 2(2\sqrt{3}r_C - r_M) \quad (14)$$

$$d_4 = \sqrt{84}r_C - 2r_M \quad (15)$$

$$d_5 = 2(3\sqrt{3}r_C - r_M) \quad (16)$$

$$d_6 = 2(6r_C - r_M) \quad (17)$$

$$d_7 = \sqrt{156}r_C - 2r_M \quad (18)$$

$$d_8 = 2(4\sqrt{3}r_C - r_M) \quad (19)$$

The interaction energy can be calculated by the pairwise summation using coulombic terms given by,

$$U_{\text{net}}(\text{kJ mol}^{-1}) = \frac{N_{\text{Av}} \times k \times \delta^2}{1000} \sum_{i,j=1}^8 \frac{n_i}{d_i} \quad (20)$$

where $k = 8.98755 \times 10^9 \text{ Nm}^2 \text{ C}^{-2}$, $e = 1.60217 \times 10^{-19} \text{ C}$, $r_{\text{Li}} = 1.52 \times 10^{-10} \text{ m}$, $r_C = 0.709 \times 10^{-10} \text{ m}$ and $N_{\text{Av}} = 6.022 \times 10^{23} \text{ mol}^{-1}$. So for partial charges on the intercalates of $0.08e$, $\delta = 0.128 \times 10^{-19} \text{ C}$, this formula becomes

Table 6 Relative repulsive interaction energy between intercalants in GICs using the pen and paper approach to count the pairwise interactions

Empirical formula	n_1	n_2	n_3	n_4	n_5	n_6	n_7	n_8	$U_{\text{net}}/U_{\text{Lic}} \delta = +0.08e$	$U_{\text{net}}/U_{\text{Lic}} \delta = +0.16e$
LiC_2	120	103	64	115	56	65	50	28	32.86	32.75
LiC_6	0	38	0	0	27	24	0	0	2.79	2.78
Li_3C_8	56	47	66	80	32	45	33	22	17.85	17.79
LiC_3	38	65	31	44	44	34	15	41	13.31	13.26
LiC'_8	0	8	8	13	0	0	0	12	1.00	1.00
LiC_8	0	0	30	0	0	21	0	17	1.50	1.49

$$U_{\text{net}}(\text{kJ mol}^{-1}) = 88.675 \times 10^{-11} (\text{kJ mol}^{-1}) \sum_{i,j=1}^8 \frac{n_i}{d_i} \quad (21)$$

and for partial charges of the intercalants of $0.16e$, $\delta = 0.256 \times 10^{-19} \text{ C}$

$$U_{\text{net}}(\text{kJ mol}^{-1}) = 3.547 \times 10^{-9} (\text{kJ mol}^{-1}) \sum_{i,j=1}^8 \frac{n_i}{d_i} \quad (22)$$

To establish an initial estimate of the pairwise sphere-sphere interactions, two researchers performed independent manual counts (*i.e.* using the pen and paper approach) using the structural image from Fig. 5. Distances were approximated by comparing the spacing between spheres relative to known lattice features. Both sets of manual counts were recorded in a separate table, allowing us to compare consistency across independent observers and identify the counts that had to be repeated to achieve agreement between the two observers.

The centre of each sphere was identified, and the distance between adjacent spheres was estimated based on the length of the C–C bond, the vertical and horizontal width of the benzene ring, and whether the distance vector was on one of the crystallographic lattice vectors or offset by one hexagonal ring of the graphite layer. By utilizing these lattice features, we were able to obtain very accurate counts of the pairwise interactions in combination with the use of a large supercell to ensure that the repulsive energy of interaction between intercalants is as accurate as needed to estimate the relative trend of stability in the these GICs, whose nearest neighbours were determined based on their surface-to-surface proximity.

With this approach, we have listed these counts in Table 5 along with the corresponding repulsive interaction energy for two partial charge values. The partial charges used on the intercalant were $0.08e$ (*i.e.* $U_{\text{net}, \delta} = +0.08e$) and $0.16e$ ($U_{\text{net}, \delta} = +0.16e$).

We also attempted to count pairwise interactions using an image analysis software that extracted the centroid coordinates of the spheres in the images in Fig. 5 and to determine the distances between the centroid Cartesian coordinates with a computer script. But these counts were not found to be correct in most cases and are therefore not listed here.

Based on Table 6, we can observe that the relative stability trends of the various GICs do not depend on the amount of partial charge on the intercalants. We also found that LiC_6 , LiC'_8 and LiC_8 are considerably more stable by almost one order of magnitude in kJ mol^{-1} than the higher intercalant density GIC's. This is in agreement with the experimental evidence that shows that LiC_6 , KC_8 , CsC_8 and RbC_8 have been prepared under ambient conditions,^{1,37,38} but the preparation of more dense phases, such as MC_3 , M_3C_8 and MC_2 , requires high pressure.

So the trend in relative internal energy of the various GICs found is



Here, we note that the stability trend calculated using the sphere-in-contact model is very reliable, as we found that the number of pairwise interactions identified by only considering a two-dimensional grid of the partial charges is as accurate as considering that the partial charge on the intercalants is smeared over the surface of a sphere. In general, we found that the repulsive energy term converges once the number of partial charges in a two-dimensional circle is larger than 8. We also found that considering a circle to distribute these partial charges, rather than a sphere, causes only a 9.2% over-estimation of the repulsive energy between two interaction circles with equally spaced partial charges around the periphery. So this trend of stabilities can be used to determine more stable GIC-based materials that still have high enough intercalant concentrations to yield high ion conductivities during charging and discharging.

Finally, we provide some trigonometric threshold values for the maximum allowed radius of the intercalant atoms for each empirical GIC formula. These values are estimates, as they are calculated based on geometric considerations within the sphere-in-contact model and indicate the radius of the intercalant atom for which there is significant overlap of the electron clouds in the various GICs. These threshold values are $2 \times r_C \times \cos 30 = 2.19 \text{ \AA}$ for MC_2 , M_3C_8 and MC_3 , $6 \times r_C = 4.27 \text{ \AA}$ for MC_6 and MC'_8 and $4 \times r_C \times \cos 30 = 4.39 \text{ \AA}$ for MC_8 . These values could be used in the rational search for other GICs with other intercalated atoms as an indicator of the thermodynamic stability of these arbitrary GICs, having these 6 different empirical formulas.

2 Conclusion

We have used the sphere-in-contact model to find various high-density empirical formulas of graphite intercalation compounds (GICs), which can serve as model systems for the development of new ion-battery materials. The model is simple and can be readily applied to any type of GIC, as long as the atomic radius of the ion is accurately estimated or the interlayer distance is known from XRD. An analysis of the geometric void space and intercalant concentration was quantified in the various models, which gives an estimate of the diffusivity of these ions during charging and discharging of the battery material (*i.e.* ion conductivity). Furthermore, we quantified the repulsive interaction energy between intercalants, which is a useful parameter to assess the thermodynamic stability of the various possible GICs. The trends in diffusivity and relative energy of the various GICs were analytically derived using the sphere-in-contact model. The threshold values of the intercalant radii are estimated for the 6 different empirical GIC formulas (*i.e.*, MC_2 , MC_6 , M_3C_8 , MC_3 , MC'_8 and MC_8), which can help in the design of new intercalated graphite-based battery materials that are more durable and simultaneously efficient charge carriers.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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