First-principles study of alkali-metal intercalation in disordered carbon anode materials†

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Graphite and non-graphitising (‘hard’) carbons are important anode materials for battery technologies. The electrochemical intercalation of alkali metals in graphite has been widely studied by first-principles density-functional theory (DFT). However, similar investigations of disordered “hard” and nanoporous carbons have been challenging due to the structural complexity involved. Here, we combine DFT with machine-learning (ML) methods to study the intercalation of alkali metal (Li, Na, K) atoms in model carbon systems over a range of densities and degrees of disorder. We use a stochastic approach to compute voltage-filling profiles, studying the three metal species side-by-side, and we analyse the ionic charges of metal atoms as a function of filling. Our study provides atomic-scale insight into the intercalation of all three alkali metals that are relevant to batteries, and it thereby makes a key step towards the DFT/ML-driven modelling of energy materials.

Introduction

Graphite and related carbonaceous materials can reversibly intercalate metal atoms to store electrochemical energy in batteries.1–3 The currently most widespread application is in Li-ion batteries (LIBs), where the formation of well-ordered intercalation compounds LiC12 and LiC6 and the “staging” mechanism have been studied.4 Interestingly, Na atoms do not intercalate into ideal graphite,6 while the larger K atoms do.7–9 First-principles computations, most widely based on density-functional theory (DFT), are a central part of modern battery research: they give atomic-scale insight into the various mechanisms at play, and today they can help to find new candidate materials for improved batteries (e.g., with increased capacity).10–12 The LiC6 intercalation compound has been studied by DFT methods for many years;13–15 a recent work explored a large space of possible structures using a DFT parameterised model.16 Potassium intercalation phases including the KC8 compound have likewise been explored by DFT.17–20 There have also been important initial steps towards the computational modelling of defective carbon structures, beyond pristine graphite and graphene. For example, the effect of vacancies on metal atom adsorption on graphene was studied, as was the intercalation of Na in defective graphite.21–23 However, more complicated systems (especially, “hard” and non-graphitising carbons) require even much larger structural models to be realistically described. Amorphous carbon24 and silicon anodes25 have been looked at with model DFT computations. Larger model system sizes are principally accessible to empirically fitted force fields,26–28 and indeed ReaxFF type force fields have been described for Li–C phases29 and Na intercalation;30 however, these methods are necessarily limited by the fixed functional form of the interatomic potential, and they allow no insight into the electronic structure.

In an initial communication,31 we have recently argued that carbon-based energy materials can be accurately described in atomistic simulations with a machine learning (ML) based interatomic potential for carbon.32 Such ML potentials perform a high-dimensional fit to complex potential energy surfaces and allow for materials modelling with close-to-DFT accuracy but require only a small fraction of the cost;33–39 we recently demonstrated the large synergy between ML and DFT methods for functionalised amorphous carbon materials.40,41 Generating the carbon structure in an ML-driven simulation bypasses the need for costly quantum-mechanical computations at runtime, making disordered anode materials such as “hard” carbons accessible to extended molecular-dynamics (MD) runs; in turn, once the carbon structures have been generated, they can be further treated with DFT to study chemical reactivity.42 Beyond carbon, recent neural-network-type ML potentials for Li–Si phases43,44 attest to the usefulness of such simulation tools. Even further, ML methods are beginning to be used in several
other areas of energy materials research, such as the screening for suitable compositions.44,45

Here, we report on a comprehensive computational survey of alkali-metal (M = Li, Na, and K) intercalation in structural models of sp²-rich disordered carbon materials that are relevant to battery research. We generate an ensemble of gradually ordered carbon structures by ML-driven high-temperature annealing simulations, and then insert metal atoms whose ordered carbon structures by ML-driven high-temperature annealing simulations, and then insert metal atoms whose undercoordinated atoms and the volume optimisation, the final mass density and atom count is specific to each cell.

Our study covers a wide parameter space of structures and densities (Fig. 1a). We use the shortest-path ring statistics as a measure for structural order;46,47 in ideal graphite, all atoms are in six-membered (“6m”) rings, whereas odd-membered rings induce curvature (e.g., the C_{60} fullerene contains 20 six-membered and 12 five-membered rings48). The presence of odd rings in disordered carbons has been observed in TEM47,48 and also suggested based on pair distribution function (PDF) analyses.49 The structures from our simulations include one (labelled 1) that has no 5/7-membered rings at all, but is much less dense than graphite, showing substantial bending of the sheets (ESI; Fig. S1†). We emphasise that the cubic cell shape is kept fixed in our simulations; we confirmed that upon full (DFT) relaxation of 1, one obtains a structure more similar to graphite, but this is not the target here. We select sets of structures that let us study trends in either ordering (along the line 1 → 4 in Fig. 1a) or density (6 → 8), while keeping the respective other property fixed. We also include one structure (5) that is relatively similar to ideal graphite but contains an extended defect (representing a “nanopore”; see below).

Methodology

Disordered carbon structures from GAP-driven simulations

A common approach for modelling disordered carbons is to start with an ideal graphite or graphene supercell in which one or a few structural defects are then introduced.50,51 In contrast, we here begin with fully disordered precursors that are partially annealed in MD runs, forming sp²-rich graphite-like regions as the simulation progresses (typically, over hundreds of thousands of time steps). The approach has been pioneered by Marks and co-workers,52,53 using the environment-dependent interatomic potential (EDIP),51 and we used a comparable protocol with an ML interatomic potential in an initial proof-of-concept study.53

Specifically, a-C precursors were generated in melt-quench simulations using the Gaussian Approximation Potential (GAP) framework54 and our recently developed carbon GAP.55 This potential has been validated in various ways, including by comparison to experimental PDFs for disordered carbon materials56 and by explicit simulation of deposition and growth of tetrahedral amorphous carbon (ta-C) films, reproducing the experimentally observed “sp³” content of ~90% in these structures.57 Each simulation started with 216 atoms per cell at mass densities between 1.5 and 2.5 g cm⁻³, using the protocol from ref. 34. All MD simulations were done using guippy (which, together with the GAP code, is available at http://www.libatoms.org) with a Langevin thermostat and a timestep of 1 fs.

The a-C precursors were gradually heated to 4000 K over 100 ps and held at that temperature for 400 ps. Compared with our previous work,11 we here annealed for longer time and at higher temperature, which induces a higher degree of ordering.50 After annealing at 4000 K, the systems were cooled to 300 K, undercoordinated atoms and long carbon chains pruned from the cells, as suggested before,51 followed by annealing at 3000 K (100 ps), cooling/pruning, and another 3000 K annealing run. Finally, cell volumes were optimised, and relaxations performed at the so-determined optimum volumes. Due to the removal of undercoordinated atoms and the volume optimisation, the final mass density and atom count is specific to each cell.

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Voltage–filling relations for disordered structures

The experimentally relevant quantity for our study is the cell voltage as a function of filling (the latter being linked to the specific capacity). Generally, the voltage U is obtained as

\[
U = \frac{-\Delta G}{nF} = \frac{G(M,C_y) - xG(M) - yG(C)}{nF}
\]

where G is the Gibbs energy for a given component, n denotes the (molar) number of electrons transferred, and F is the Faraday constant. In computational practice, the above expression is normally approximated as

\[
U = -\frac{1}{x} \left[ E_{DFT}(M,C_y) - xE_{DFT}(M) - yE_{DFT}(C) \right]
\]

where all total energies E are obtained from DFT computations at the same level. Note that this approach is formally based on energies at zero kelvin, and does therefore not take temperature into account; the validity of this approximation has been shown before.11 In this work, there are no crystallographically well-defined staging compounds with integer x and y (such as in ordered LiC₆₀); instead, we have to sample a sufficiently large ensemble of candidate adsorption sites (Fig. 1b). We start with 20 independent computations at small x and reduce the number of sampled cells to 10 and then to 5 at larger x, as the scatter between points decreases (Fig. 1c). The idea of exploring possible structures in a stochastic way, with only basic (physically motivated, such as hard-sphere) constraints is reminiscent of the Ab Initio Random Structure Searching (AIRSS) technique60,61 which has been widely used for battery materials.62-64

Computational details

DFT computations were performed using the projector augmented-wave method65 as implemented in VASP 5.4.4.66,67 Exchange and correlation were described using the optB88-vdW functional,68-71 which takes van der Waals (vdW) interactions into account. This level of theory was recently used to fit a GAP for pristine graphene,72 and computational parameters as in that work were used as appropriate. We confirmed that the
chose dft method and settings accurately describe the lattice
parameters of the experimentally known crystalline M@C phas
es (see esi for details†).

initially, the atomic coordinates in all candidate structures
were relaxed using dft until residual forces fell below 0.01 eV
Å−1. in these computations, reciprocal space was sampled at the
Γ point, and an electronic smearing of σ = 0.2 eV and a cut-off
energy of 250 eV were used; cell shape and volume were kept
fixed (see above). Then, for the optimised structures, more
accurate single-point computations were performed, employing
a grid of 3 × 3 × 3 k-points, σ = 0.1 eV, and a cut-off energy of
500 eV. Convergence tests confirmed that increasing the grid to
5 × 5 × 5 k-points changed the computed voltage values by no
more than 0.01 V (esi†).

Projected electronic densities of states (DOS) were obtained
from the self-consistent wavefunctions by analytic projection
into a local auxiliary basis set of valence s and p orbitals, using
the LOBSTER software (http://www.cohp.de),73,74 which has
recently been applied to carbon materials for battery applica
tions.13,75 Charges on atoms were computed using the Löwdin
scheme86 as implemented in LOBSTER.77

results and discussion

intercalation in disordered carbon structures

With the optimised carbon structures 1–8 in hand (Fig. 1a), we
proceed to simulate the insertion of metal atoms. DFT allows us
to investigate arbitrary guest species directly—in this case, it is
straightforward to add Li, Na, and K atoms in parallel runs. Due
to the disordered nature of the structures, we need to sample
several randomly chosen configurations; an example is given in
Fig. 1c. In the latter figure, we also include experimental data for
comparison: these depend strongly on the nature (e.g., the
synthesis pathway) of the specific carbon material, and there
to the interpretation and comparison to DFT can be semi-
quantitative at best. That being said, we argue that the
comparison of different model systems and the computed
voltage–filling relations allows for useful insight that would be
inaccessible without the large diversity of carbon structures we
are able to sample here.

To provide a point of reference, we begin by discussing metal
adsorption energies in a simpler system: namely, on selected
high-symmetry sites of pristine and defective graphene (Table
1). Such studies have been done before,47,76–80 but they are here
repeated using the same dft framework that we will use for the
disordered structures, for full consistency. On a pristine gra
phene sheet, adsorption on the “hollow” site is always preferred
over the “top” and “bridge” sites; this preference is much more
strongly pronounced for Li than for the larger Na and K atoms.
Among the three metals, the absolute adsorption energy (i.e.,
the stabilisation of an adsorbed atom) is lowest for Na, in accord
with the poor intercalation propensity of Na in graphite.46 Adsorption on a Stone–Wales (SW) defect and especially on
a vacancy site is visibly more favourable than that on pristine
graphene; again, the absolute stabilisation is largest for Li and
smallest for Na. Hence, structural defects (where they occur) will play a role early on in the adsorption process.

We now return to the central subject of this work, our disordered structures 1–8, focusing on Li intercalation for the moment (Fig. 2). The DFT results can be classified according to the properties of the underlying carbon framework:

(i) 1 is a structure made of sheets with ideal graphite-like topology (6m rings throughout), but with substantial non-planarity. We find that bending of carbon sheets alone, which 1 represents, is not a necessary or sufficient criterion for intercalation: almost all computed data points are at negative voltage (i.e., unfavourable insertion), and so the scan was terminated after a few steps.

(ii) 2–4 vary in their count of odd-membered rings, but they all have a similar initial density of 1.3–1.4 g cm\(^{-3}\), typical of porous carbon materials. The initial samples (\(x < 0.2\)) show a pronounced variation in maximum voltages, but once the structures approach larger filling (\(x > 0.5\))—that is, once the structural defects have been saturated—, their computed voltage-filling relations are quite similar, falling in between the two experimental datasets\(^{24,46}\) (red and orange lines in Fig. 2) in all three cases.

(iii) 5 is a structure with an open pore. Initially, the Li atoms readily intercalate, indicated by highly positive voltages (vs. Li\(^+\)/Li; favourable adsorption). Overall, the datapoints are in reasonable agreement with the dataset by Legrain et al. obtained for intercalation into amorphous carbon,\(^{24}\) although a truly quantitative comparison will require system sizes of much more than 200–250 atoms and the assessment of different pore shapes and sizes.

(iv) 6–8 are structures with varying density. They seem to have a maximum in voltages at intermediate density, at a value slightly lower than that of graphite (7; cf. Fig. 1a), whereas at too high density of the carbon framework (8) intercalation becomes distinctly less favourable.

Our simulation cells sample a wide range of structural motifs, such as odd-membered rings and open pores, which are expected to facilitate the adsorption and clustering of alkali metal atoms. The idealised computations in Table 1, in accord with previous literature,\(^{23,47}\) confirm that structural defects are preferred adsorption sites: these sites provide additional capacity and would result in high voltage (vs. Li\(^+\)/Li) when using carbon as anode. The DFT results for 2–4 suggest that filling of such defects at the initial stage (\(x < 0.2\)) could have a significant effect on the voltage. We emphasise that these computations sample the (optimised) insertion structures at a given \(x\), but not the dynamics of the entire gradual process: for example, defect
sites on which Li is strongly bound can “trap” Li atoms, leading to an irreversible loss of capacity. To fully understand the reversibility, large-scale MD simulations of the charging/discharging and diffusion mechanisms are required. ML potentials could be suitable tools for such tasks,\textsuperscript{46} but the development and validation of these far exceeds the scope of the present paper.

Moving in the vertical direction in Fig. 1a and comparing structures with a similar number of 5m and 7m rings (viz., 4, 6, 7, 8), but different density, clearly emphasises the role of the latter for intercalation. Low-density carbons exhibit a large space between carbon layers, making the adsorption of ions more similar to that on ideal graphene or, as recently observed, in bilayer graphene.\textsuperscript{81} On the contrary, for dense forms, distances between the layers are smaller and intercalated ions will begin to experience repulsion, causing the DFT voltage points to drop below zero for 8. Our data also suggest that the latter structure is better comparable to the more ordered material characterised by Stevens and Dahn (orange in Fig. 2),\textsuperscript{46} rather than to the highly disordered (ball-milled) amorphous samples of Legrain et al. (red in Fig. 2). Summarising thus far, the density appears to be an important factor to be considered when designing disordered carbon materials for energy storage.

Having studied Li intercalation in some detail, we now look at the heavier homologues, Na and K. Exploratory computations showed that not all eight model carbon systems are relevant in this case: intercalation in 1 is not favoured, similar to the case of Li (Fig. 2a), and the dense structure 8 does not readily accommodate the larger ions (see Fig. S2 in the ESI).\textsuperscript{†} We therefore focus on selected structural models at densities commensurate with different carbonaceous materials. The results are collected in Fig. 3.

At low densities, the predicted voltage–filling relations are reminiscent of those for Li; introducing structural disorder in the form of 5m/7m rings (which is small in 2 but large in 4) in our models has a very limited effect on the overall shape of the computed voltage profile. For Na intercalation (Fig. 3a), both 2 and 4 lead to a substantially higher voltage and capacity than the experiment to which we compare, from \( x \approx 0.2 \) onwards. They are therefore not suitable proxies for modelling this specific material: indeed, super P carbon materials (\( \approx 1.6 \text{ g cm}^{-3} \)) are more disordered and slightly denser than the simulated models. There is a discernible variation in Na intercalation at small filling (i.e., the voltage ranges differ in 2 and 4 for \( x \approx 0.2 \)); no such effect is seen for K (Fig. 3c). The predicted voltages, in all these low-density cases, remain positive throughout the range of \( x \) values surveyed, exceeding the (hypothetical) limit of “NaC\(_6\)” (\( x = 1.0 \) in Fig. 3a) and the experimentally known composition KC\(_8\) (\( x = 1.0 \) in Fig. 3b). The presence of voids, therefore, is expected to principally enhance the uptake of the heavier alkali atoms.

For structure 7, which has a higher density (\( \approx 2.1 \text{ g cm}^{-3} \)) approaching that of graphite, the slope of the Na voltage–filling data agrees better with experiment (Fig. 3b). We also explored K intercalation in 7, where the voltages reach zero (indicating unfavourable intercalation) at a K content of around half that of the ideal crystalline compound KC\(_8\) (Fig. 3d). For future experiments on K-ion battery anodes even more so than for Na, lower-density carbons may be of interest.

Concluding the discussion of computed voltage–filling relations, it should be noted that a solid electrolyte interphase (SEI) will form between the carbon anode and an organic electrolyte during the first charge/discharge cycle.\textsuperscript{8,83,84} As a consequence of SEI formation, the alkali ions now need to pass through the

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Fig. 3 Voltage–filling plots as in Fig. 2 but now for the intercalation of (a and b) Na and (c and d) K into structures 2, 4, and 7, respectively. Experimental data for Na intercalation (red dashed line) are taken from Legrain et al. (ref. 24); we do not know of reports on the reversible insertion of K in comparable amorphous carbon materials.
layer to intercalate in the carbon materials; the precise nature of this process is expected to differ between Li, Na, and K. The SEI layer could be considered as a resistor and its presence would slightly lower the voltage curve compared to our prediction. Solid-state NMR could be used to probe the SEI, and elucidating the mechanisms of how ions pass through the layer could benefit from further (DFT- or ML-driven) MD studies.

Electronic structure

With the optimised atomic structures available, electronic-structure computations were carried out to better understand the intercalation properties. We compare, in Fig. 4, atomically resolved electronic densities of states (DOS) for the three alkali metals, showing three selected datasets for each, from low to high filling. Due to the presence of defects and disorder, carbon systems from such simulations exhibit a finite DOS at the Fermi level. Initially (left-hand side), the DOS contributions by the metal atoms are all above the Fermi level (dashed line); this corresponds to an unfilled s valence orbital and therefore to an ionic state in all three cases (Li+, Na+, K+). With increasing filling, larger and larger contributions below the Fermi level are seen in the projected DOS for the metal atoms (middle and right-hand-side panels in Fig. 4a–c). Such mechanisms have been previously discussed for Li on graphene and Na in a “porous” carbon model system. Our present computations, starting from the same carbon frameworks for Li, Na, and K (and therefore ensuring direct comparability), suggest the crossover from ionic to metallic nature to be a universal feature of all three alkali-metal species being intercalated into carbon materials.

Fig. 4 Electronic densities of states (DOS), computed using DFT and atomically resolved by projection into a local basis (methods), providing a fingerprint of electronic structure at various degrees of filling. Projections onto the C atoms (grey) and metal atoms (blue) are shown for (a) Li, (b) Na, and (c) K, respectively. The Fermi level is set as energy zero and indicated by a dashed line.

Charges on atoms: ionic versus metallic nature

It has been deduced from operando NMR experiments that charge is gradually transferred during Na insertion in disordered carbons, starting with Na+ ions and then moving towards Na0. To supplement these findings with first-principles simulations, we compute charges on atoms; this largely extends our earlier proof-of-concept, where we studied a few instances of Na intercalation. An example, now for the case of Li, is given in Fig. 5a: atoms adsorbed near the edge of the pore mainly reside on the “hollow” sites of 6m and odd-membered rings (consistent with the data for idealised graphene in Table 1), and their charges are on the order of 0.8, close to ideal Li+. The majority of atoms is found near the edge of the nanopore, in which case the charges are somewhat smaller but still clearly supporting a partially ionic nature of Li. In the centre of the pore, finally, we observe one Li atom that is surrounded by many others, but that is not close to any C atom of the host framework. In this case, the computed charge is 0.28, bringing the electronic nature of this atom very close to the metallic state.

A more quantitative view is enabled by collecting charge values over several atomic environments, at various degrees of filling (x in LixC6) and comparing these results side-by-side (Fig. 5b). In accord with the PDOS data that we have discussed above, the charge distributions gradually shift down and lead to an apparently bimodal distribution, with one peak near 0.8 (persisting even at very high filling, close to LiC6), and one peak building up between Löwdin charges of 0.6 and 0.3. This splitting suggests that there are distinctly different groups of Li atoms in carbon anode materials. However, this distribution alone does not yet reveal the structural and chemical origins of these groups.

We therefore use the Smooth Overlap of Atomic Positions (SOAP) kernel, a structural similarity measure initially used for GAP fitting but having more general implications, to analyse local structures. SOAP quantifies the similarity of two atomic environments i and j on a scale from kij = 0 (fully dissimilar) to kij = 1 (identical up to symmetry operations and within a specified cut-off radius), where the SOAP kernel kij is defined in ref. 88; parameters are taken from ref. 81. Visualising the so-obtained (dis)similarity between atomic environments can yield useful information. For example, a technique called clustering can be employed to identify the most relevant chemical sites in amorphous structures, as shown by Caro et al. for...
These approaches are examples for the wider area of “unsupervised” machine learning, in which one aims to extract information from unlabelled datasets; the usefulness of such techniques for chemistry has been highlighted very recently. In Fig. 6, we visualise the structural distances and thus the relationships between different environments of Li atoms in DFT-optimised structures at various degrees of filling. We compute the distance $d$ of sites from one another, defined as

$$d(i,j) = \sqrt{2 - 2k_{ij}},$$

and use a dimensionality reduction technique to draw a 2D map that represents these distances. We then colour-code the data points by (DFT-computed) charges on the respective atoms, aiming to discover not only structural but structure–property relationships.

Interestingly, the Li environments appear to fall not into two groups (as the apparently bimodal distributions in Fig. 5b might have suggested), but into three groups, based on the local environments involved. We observe (1) isolated atoms, which the colour-coding in Fig. 6 confirms to have an almost fully positive charge, (2) clustered atoms with approximately half a unit charge, with a gradual transition between the two, and then, structurally far away, (3) metallic-like atoms with charges close to zero. It is expected that such analysis techniques will be useful in the future when studying disordered carbons where traditionally used labels such as the “hollow”, “top”, and “bridge” adsorption sites (Table 1) cannot be easily applied due to the structural complexity and vast amounts of data; instead, kernel-based distance maps can be generated in an automated fashion and without the need for pre-defining any structural motifs. We stress that they are not restricted to carbon but could prove useful for other disordered battery materials as well.

**Conclusions and outlook**

Machine learning and DFT methods have been combined to study the intercalation of alkali metal atoms in model carbon systems, comparing all three species (Li, Na, K) that are relevant to batteries. Performing up to 20 independent computations for
each system and step of filling makes it possible (and is, in fact, required) to gain stochastic insight into the atomic-scale processes, charges on atoms, and the mechanisms by which metal ions are inserted. These mechanisms are reflected in predicted voltage–filling relations (providing a direct link to experiments within the limits of finite model system sizes). Having access to representative structures also makes it straightforward to compute and analyse electronic-structure fingerprints (such as projected densities-of-states and atomic charges), which we have here presented for all three metals side-by-side.

It is hoped that the simulation protocols and structural data provided in this work can directly enable more detailed DFT studies in the future—selecting, from the wide parameter space of disorder and densities, the most representative model system to represent a given problem (such as a disordered region in “hard” carbons). The strategy outlined here could thus become a useful general approach to understand, and ultimately, to optimise, disordered carbon materials for future battery technologies.

Data access statement

Data supporting this publication are provided as ESL† further data are available at https://doi.org/10.17863/CAM.42087.

Conflicts of interest

There are no conflicts to declare.

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