

Edge-Propagation Discharge Mechanism in CF_x Batteries—A First-Principles and Experimental Study

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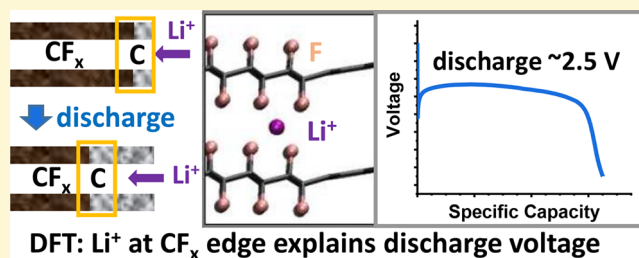


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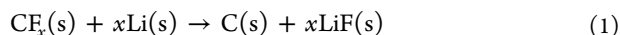
ABSTRACT: Graphite fluoride (CF_x) cathodes coupled with lithium anodes yield one of the highest theoretical specific capacities (>860 mAh/g) among primary batteries. In practice, the observed discharge voltage (~2.5 V) is significantly lower than thermodynamic limits (>4.5 V), the discharge rate is low, and so far Li/CF_x has only been used in primary batteries. Understanding the discharge mechanism at atomic length scales will improve practical CF_x energy density, rate capability, and rechargeability. So far, purely experimental techniques have not identified the correct discharge mechanism or explained the discharge voltage. We apply density functional theory calculations to demonstrate that a CF_x-edge propagation discharge mechanism based on lithium insertion at the CF/C boundary in partially discharged CF_x exhibits a voltage range of 2.5 to 2.9 V—depending on whether solvent molecules are involved. The voltages and solvent dependence agree with our discharge and galvanostatic intermittent titration technique measurements. The predicted discharge kinetics are consistent with CF_x operations. Finally, we predict some Li/CF_x rechargeability under the application of high potentials, along a charging pathway different from that of discharge. Our work represents a general, quasi-kinetic framework to understand the discharge of conversion cathodes, circumventing the widely used phase diagram approach which most likely does not apply to Li/CF_x because equilibrium conditions are not attained in this system.



I. INTRODUCTION

Graphite fluoride has the chemical formula CF_x with $0 < x \leq (1 + \delta)$. When fully fluorinated ($x \sim 1$), CF_x cathodes exhibit one of the highest theoretical specific capacities (864 mAh/g) among cathode materials,¹ and they have been commercialized as primary lithium battery cells.^{2,3} CF_x is typically synthesized by enforcing chemical reactions between F₂ gas and graphite or other forms of conductive carbon at elevated temperatures.^{4–7} Idealized models of $x = 1$ samples have layers of CF with each carbon atom chemically bonded to three other C atoms and one F atom (Figure 1a–b). The registry between adjacent sheets has been predicted to have minimal effect on the total energy.⁸

Li/CF_x batteries discharge via the overall reaction



where “(s)” denotes the solid state. Using thermodynamic data and eq 1, the average theoretical voltage is estimated at 4.57 V at $x = 1$; it is even higher at smaller x , reaching 5.07 V at $x = 0.7$.¹ In practice, the usable energy density is significantly lower than expected from thermodynamics. Li/CF_x batteries discharge at a plateau voltage of $< \sim 2.5$ V at rates of 0.05 C or less (Figure 2a,c,d). The observed voltage variation is a small fraction of a volt when using different carbon precursor materials,⁹ or electrolytes—including both organic sol-

vents,^{10,11} solid electrolytes,¹² and liquified gas electrolytes (Figure 2d).^{13,14} Galvanostatic intermittent titration technique (GITT) measurements, which should circumvent most kinetic limitations, have reported CF_x discharge voltages below 3.1 V (Figure 2b).¹⁵ CF_x materials with more “ionic” C–F bonds, synthesized at x values substantially lower than unity, are reported to yield slightly higher voltage plateaus and higher discharge rates at the expense of lower overall capacities.^{16–18} Disordered/nanoscale carbon precursors also yield a rate capability improvement.^{19,20} Unlike Li/CF_x, Na/CF_x batteries have been demonstrated to be rechargeable.^{21–24}

Achieving performance near the ideal theoretical values as predicted by thermodynamics will significantly broaden the application space and impact of CF_x batteries. A detailed elucidation of the CF_x discharge mechanism at the atomic length scale is required in order to ultimately achieve increased voltage windows, higher energy densities, higher power capability, and improved rechargeability. Several discharge

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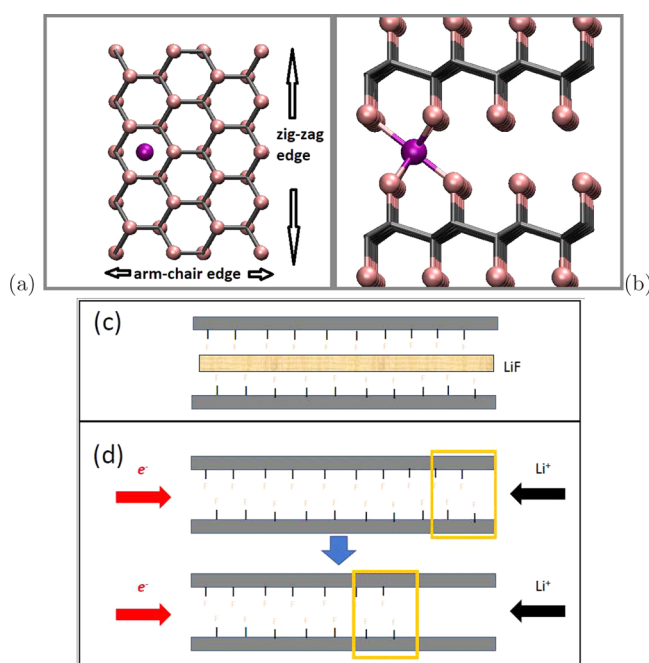


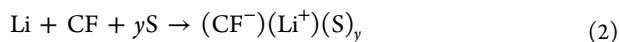
Figure 1. (a–b) Two views of CF_x sheets at $x = 1$; zigzag and arm-chair edges (in analogy with graphite) are indicated. A Li atom is hypothetically inserted between two CF_x sheets. C, F, and Li atoms are depicted as gray, pink, and purple spheres or sticks. (c–d) Schematics of the LiF intermediate phase and edge-propagation CF_x discharge mechanism, respectively. Yellow lines highlight local active discharge regions. Black sticks are C–F bonds.

mechanisms have been proposed to explain the voltage profiles; they differ by whether intermediate phases, edge planes, and/or solvent molecules are involved.

Mechanism A: Two Phase Behavior. In the absence of intermediate phases, the discharge should exhibit two-phase behavior, and the observed voltage should follow eq 1.^{25,26} The reason for the discrepancy between the thermodynamic (>4.57 V) and observed (~ 2.5 V) discharge voltages is then ascribed to slow kinetics and/or nanosize effects associated with LiF/NaF products. One argument against such a two-phase behavior is that eq 1 predicts an increase of the equilibrium voltage \mathcal{V}_i as discharge proceeds (x decreases),¹ which has not been observed (Figure 2).

Mechanism B: Intermediate Phase. Alternatively, an intermediate phase has been invoked to explain the 2.5 V plateau. This may be a ternary phase such as CLi_xF ,²⁷ which can be a thin sheet of one or more LiF layers intercalated between CF_x or C sheets (Figure 1c).^{24,27} In this case, eq 1 does not govern the discharge voltage. Changing CF_x lattice constants with discharge have been reported in *in situ* X-ray analysis,^{28,29} which may suggest such a LiF intercalation structure. However, Mechanism (B) appears less consistent with CF_x not in stack-like configurations, e.g., those synthesized using carbon nanotube precursors.

Mechanism C: Edge-Mediated. Another candidate for the intermediate phase is a solvent-coordinated Li^+ complex,^{3,30}



where “S” is a solvent molecule. Such a mechanism necessarily requires an edge-propagation rather than bulk-phase reaction pathway. Edge-propagation mechanisms are attractive because

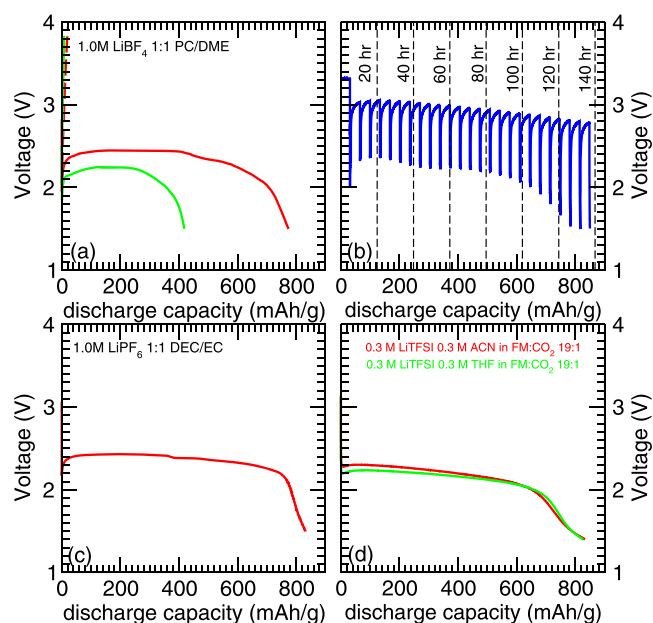


Figure 2. (a) Galvanostatic discharge and charge of CF cells with PC/DME/ $\text{Li}^+/\text{BF}_4^-$ electrolyte. Cells were left at open circuit voltage for 20 h and then cycled at a rate of C/20 (red) or C/5 (green). The plot shows that faster rate results in a lower discharge capacity and that neither cell shows any electrochemical reversibility (attempted recharge in dashed lines); $\text{CF}_{1.09}$ is the initial composition. (b) GITT of a cell with the same build as those in panel (a), CF cell using a 1.789 mA current pulse, corresponding to a discharge rate of C/20, with a 30 min pulse time and 5 h rest. The final capacity of the GITT measurement is 825.90 mAh/g. (c) Galvanostatic discharge profile with DEC/EC/ $\text{Li}^+/\text{PF}_6^-$ electrolyte. (d) Galvanostatic discharge of CF cells with two liquified gas electrolytes (LGE) at C/20 rate; $\text{CF}_{1.05}$ is the initial composition.

they would be consistent with an extended plateau voltage region independent of the extent of the state-of-charge (x). This is because if the discharge behavior only depends on the local configuration (Figure 1d), to a first approximation the spatial location of discharge, dependent on x , would not affect the discharge voltage. This is consistent with the appearance of a near constant voltage discharge plateau (Figure 2a). However, the intermediate phase associated with this mechanism would be small and hard to detect via X-ray diffraction.^{28,29}

Mechanisms (B) and (C) are not mutually exclusive. Strictly speaking, Mechanism (B) does not completely specify a discharge pathway, in terms of the order in which C–F bonds are broken. If thermodynamic equilibrium is assumed, i.e., C–F bonds are broken in ascending order of bond energies, Mechanism (B) may be consistent with an overall, lower average discharge voltage than 4.57 V, but would fail to explain why the observed discharge voltage does not increase with decreasing x (Figure 2), as thermodynamics would predict.¹ However, when combined with Mechanism (C), the formation of a CLi_xF phase (Figure 1c) may follow edge-mediated C–F bond-breaking events.

So far, purely experimental efforts have not definitively determined the mechanism. Computational work will shed light on Mechanisms (A)–(C). Regarding Mechanism (A), two-phase-like solid state conversion reactions are well understood and routinely modeled using a phase-diagram approach.^{31,32} The effect of nanosized charge/discharge

Table 1. Computational Details of Representative Simulation Cells^a

system	dimensions	stoichiometry	k-sampling	Figure
zigzag	6.10 × 2.60 × 32.00	C ₁₈ F ₂₀	3 × 10 × 1	
zigzag	6.10 × 5.21 × 32.00	C ₃₆ F ₄₀	3 × 5 × 1	
zigzag	6.10 × 7.81 × 32.00	C ₅₄ F ₆₀	3 × 3 × 1	
arm-chair	6.10 × 4.63 × 32.00	C ₃₆ F ₄₀	3 × 6 × 1	
arm-chair	6.10 × 9.65 × 32.00	7 ₂ F ₈₀	3 × 3 × 1	
zigzag/Li ⁺	12.20 × 10.40 × 32.00	C ₁₄₄ F ₁₂₈ Li	2 × 5 × 1	Figure 3a
zigzag/Li ⁺	12.20 × 10.40 × 32.00	C ₁₄₄ F ₈₀ Li	2 × 5 × 1	Figure 3f
zigzag/Li ⁺	12.20 × 20.80 × 32.00	C ₂₈₈ F ₂₅₆ Li	2 × 5 × 1	
arm-chair/Li ⁺	12.20 × 9.27 × 36.00	C ₁₄₄ F ₁₁₂ Li	2 × 3 × 1	Figure 6a
arm-chair/Li ⁺	12.20 × 9.27 × 44.00	Au ₄₀ C ₁₄₄ F ₁₁₂ Li	2 × 3 × 1	Figure 6b
zigzag/Li ⁺	12.20 × 10.40 × 44.00	C ₁₄₄ F ₂₀₀ Li ₇₂	2 × 5 × 1	Figure 7a

^aThe dimensions are in units of Å³.

products has been addressed within the framework of phase diagram calculations to explain the discrepancy between bulk phase thermodynamics predictions and observed battery discharge profiles.^{24,33} However, nanosizing is usually insignificant for particle size on the order of 10 nm, which are the dimensions of LiF discharge products.²⁶ Further experiments are needed to ascertain the LiF size distribution. Furthermore, the phase diagram approach assumes equilibrium conditions and reversible reactions. While this is true of many conversion cathode materials,^{31,32} rechargeability associated with eq 1 has yet to be demonstrated in any electrolyte, which suggests that equilibrium conditions do not apply. In the Supporting Information (SI) (Sec. S2), we further report that density functional theory (DFT) electronic structure calculations predict a barrier for the exchange of two neighboring F-vacancies on a CF sheet that is far too large to permit diffusion, consistent with previous bond-strength calculations.^{34,35} This shows that different C–F bond configurations in CF_x materials are not at equilibration with each other.

Regarding Mechanisms (B) and (C): in this work, we apply DFT to show that Mechanism (C), even without solvent molecules, gives good agreement with experiments. Motivated by edge-initiated discharge in graphite used as lithium ion battery anodes,^{36–38} we examine edge-propagation CF_x discharge (Figure 1d). We find that Li or Na intercalation into interfacial sites between insulating CF and conductive, defluorinated graphite regions constitutes a small “intermediate phase” most consistent with the observed CF_x discharge voltage plateau (Figure 2). This intermediate dovetails with classic “interfacial charge storage” behavior.^{39,40} Li insertion is followed by defluorination at the CF/C interface and then further Li insertion, leading to quasi-one-dimensional, row-by-row defluorination and subsequent formation of LiF. LiF formation energetics does not determine the voltage. In addition to CF_x stacks, our model is applicable to CF_x flakes and fluorinated carbon nanotubes with small curvatures, as long as their discharge involves row-by-row defluorination. In this work, we adopt idealized, defect free, partially defluorinated CF_x with zigzag and arm-chair edges as models. Defects in carbon sheets and other heterogeneity (e.g., C–F vs C–F₂ distributions^{41–43}) also affect CF_x battery operations; these complexities will be deferred to future modeling work.

Our calculations also consider Li/CF_x recharge and discharge rates. Regarding solvent effects: given the large variation in the binding energies between Li⁺ and different solvent molecules we will discuss, the solvent dependence of discharge voltage reported in the literature, on the order of 0.2

V, appears surprisingly small and requires further elucidation.^{30,44} This will be addressed by adding solvent molecules at CF_x edge sites in DFT simulations and comparing to our measurements done in two solvents. A significant amount of DFT modeling work on CF_x has been reported.^{8,35,45–54} Few of them deal with CF_x edges; however, this prior research provides significant guidance and starting structures for the work discussed below.

II. METHOD

To calculate energies associated with voltages (eq 1 and 2), we apply static DFT calculations with periodically replicated simulation cells, the Vienna Atomic Simulation Package (VASP) version 5.3^{55–58} and the Perdew–Burke–Ernzerhof (PBE) functional.⁵⁹ A 400 eV plane-wave energy cutoff is imposed, except that a 500 eV cutoff is used when optimizing simulation cell sizes. We adopt a 6.1 Å, CF_x intersheet spacing, similar to ref 8.

Our DFT simulation cells represent stacked, partially defluorinated CF_x sheets with sharp interfaces between the fully defluorinated graphene and fully fluorinated (CF) regions. The simulation cell sizes correspond to CF, not graphite, lattice constants; hence strain develops in the defluorinated region.⁴⁶ Representative simulation cell dimensions, stoichiometries, and Brillouin zone sampling settings are listed in Table 1. Other calculations involve variations on these cells. All simulation cells considered are overall charge-neutral. The dipole moment correction is applied in all but a few calculations which do not contain a vacuum region.⁶⁰ This correction only avoids charge/image-charge interactions in the *z* direction perpendicular to the CF/C interface. When the simulation cell exhibits significant dipole moments, systematic increase of cell size in the lateral directions is still necessary to converge relevant energy differences. Spin-polarized DFT is used except for certain arm-chair edge calculations with an even number of electrons, where non-spin-polarized DFT gives the same result. A few calculations apply the generally more accurate DFT/HSE06 functional.^{61–63} The dispersion-corrected optB86b-vdW functional is also tested in some cases.⁶⁴ The electronic voltage is determined using the work function approach, which is possible in the absence of liquid electrolytes.⁶⁵

We also perform finite temperature *ab initio* molecular dynamics (AIMD) simulations of a small Li cluster in contact with zigzag or arm-chair edges. These are short-circuit condition simulations which help motivate the sharp CF/C boundaries used in *T* = 0 K DFT simulation cells. A Nose thermostat imposes *T* = 350 K conditions. The simulations adopt Γ -point Brillouin zone sampling; other settings are the same as those discussed above. The zigzag edge AIMD cell has a 17.93 × 13.01 × 28 Å³ dimension and a C₁₅₀F₁₈₀Li₂₁ stoichiometry. The arm-chair edge simulation cell has a 18.30 × 13.51 × 28 Å³ dimension and a C₁₂₆F₁₄₄Li₂₁ stoichiometry. The results are described in the SI.

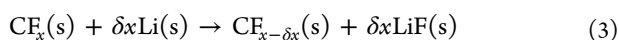
Experimental details are discussed in the SI.

III. RESULTS

III.A. Experimental Results. Discharge and GITT profiles for CF_x cells with propylene carbonate (PC)/1,2-dimethoxyethane (DME)/lithium tetrafluoroborate (LiBF_4) electrolytes are depicted in Figure 2a and b. They are similar to results reported in the literature for Li/CF_x batteries.^{66,67} Figure 2a shows that the discharge voltage profile exhibits a plateau around 2.4 V at the C/20 rate; discharge voltage and capacity become much more limited at the faster C/5 rate. Recharging does not occur at either rate when an upper voltage cutoff of 4.0 V is imposed. The GITT results (Figure 2b) show that the highest observed discharge voltage after the initial pulse is ~ 3.05 V. The instantaneous diffusion constants associated with Figure 2b are depicted in the SI (Figure S1). Omitting the first two pulses, we estimate the average Li^+ diffusion constant to be $4.47 \times 10^{-12} \text{ cm}^2/\text{s}$ assuming Li^+ enters the cathode via an ion-insertion pathway (not just a surface reaction). This value is 2 to 3 orders of magnitude slower than in commercial secondary lithium-ion battery materials, but it does not appear forbiddingly slow.^{68–70} The galvanostatic discharge profile of an electrolyte with ethylene carbonate (EC)/diethyl carbonate (DEC)/lithium hexafluorophosphate (LiPF_6) (Figure 2c) is similar to that without EC (Figure 2a).

Galvanostatic discharge data of two fluoromethane (FM)-based liquified gas electrolytes (LGE), with lithium bis(trisfluoromethanesulfonyl)imide (LiTFSI) salt, CO_2 additive, and either 0.3 M acetonitrile (ACN) or 0.3 M tetrahydrofuran (THF), show lower discharge voltages compared with carbonate-based liquid electrolyte at the same C/20 rate (Figure 2d). This solvent variation will be compared with DFT studies below.

III.B. Intrinsic Defluorination Thermodynamics Does not Explain Voltage. The equilibrium voltage \mathcal{V}_i associated with a small defluorination increment δx along a particular defluorination pathway,



is given by

$$e|\mathcal{V}_i = -[E(\text{CF}_x) - E(\text{CF}_{x-\delta x})]/\delta x + E(\text{LiF}) - E(\text{Li}) \quad (4)$$

where the energies $E()$ all refer to those of solid phases. The larger a C–F bond energy ($[E(\text{CF}_x) - E(\text{CF}_{x-\delta x})]/\delta x$) for a particular carbon atom, the lower is the voltage required to defluorinate that atom. Note that more positive \mathcal{V}_i and more negative energy changes mean more favorable reactions with Li. We stress that \mathcal{V}_i can only be realized in experiments if the corresponding reaction step occurs under equilibrium conditions.

First we discuss the energetics of bulk phase CF_x defluorination without metal content in the simulation cell. In this formulation, the effect of Li^+ is solely manifested in the LiF formation energy. This corresponds to Mechanism A. Similar calculations have been applied in previous DFT studies of CF_x batteries.^{8,45–53} No CF_x edge or solvent molecule is included in this approach. Using the PBE, HSE06, and optB86b-vdW functionals, the equilibrium voltages associated with eq 1 at $x = 1$ (i.e., averaging the voltage defluorinating the entire CF material) are found to be $\mathcal{V}_i = 4.38, 4.40,$ and 5.16 V, respectively. Periodically replicated CF_x or graphene sheets instead of 3-dimensional structures for both “CF” and “C” in eq 1 yield similar results, except that the optB86b-vdW

functional voltage is slightly lowered to 5.11 V. The PBE and HSE06 functionals are in closest agreement with thermodynamic data,¹ and the computationally less costly PBE is applied for the remainder of this work.

We also consider starting at the $x \rightarrow 1$ limit and removing two neighboring F atoms from a periodically replicated CF sheet via eq 4. A $\text{C}_{48}\text{F}_{48}$ model is used (i.e., $\delta x = 1/24$, defluorinating a small portion of the CF). Equation 3 coupled with eq 4 yields $\mathcal{V}_i = 2.86$ V, which is significantly lower than the average value of 4.38 V. See Table 2. This PBE-predicted

Table 2. Computed Voltages (\mathcal{V}_i) at Different Configurations^a

system	\mathcal{V}_i	figure	notes
bulk CF_x	4.38 V	NA	averaged over $x < 1$
bulk CF_x	2.86 V	NA	at $x = 1$ only
bulk $\text{CF}_x + \text{Li}$	0.93 V	Figure 1a–b	insert Li
zigzag	2.62 V	Figure 3a	insert Li
zigzag	1.45 V	Figure 3e	insert second Li
zigzag	2.56 V	Figure 3f	further defluorination
zigzag	2.90 V	Figure 5a	with EC
zigzag	2.49 V	Figure 5b	with FM
zigzag	2.66 V	Figure 5d	sheet, with EC
zigzag	2.25 V	Figure 5f	sheet, with FM
arm-chair	1.49 V	Figure 6a	insert Li
arm-chair	1.81 V	Figure 6b	with Au(111)

^aBulk defluorination voltages follow eq 1 or 4 while Li-insertion voltages follow eq 5. EC and FM are ethylene carbonate and fluoromethane, respectively.

trend, whereby \mathcal{V}_i increases with the state of the discharge (smaller x), is qualitatively consistent with thermodynamic data¹ but is inconsistent with observed electrochemical discharge voltage profiles (Figure 2). We have not considered intermediate values of x partly because of the multiplicity of possible defluorination configurations with complex energy landscapes⁴⁶ and partly because our edge-propagation mechanism described below provides a more physical, quasi-kinetic pathway for the sequence of F atom to be removed, than a global optimal energy criterion.

III.C. Li-Insertion Energetics at the Zigzag CF/C Interface. During CF_x discharge, Li^+ should be present at the CF_x edge facing the electrolyte (right side of Figure 1d). Simultaneously, an e^- is injected from the current collector (not explicitly included in our DFT model) on the left side. The added e^- moves infinitely fast in ground state DFT calculations; therefore operationally these two charge injection steps are consistent with adding a Li atom on the surface facing the electrolyte. In the SI (Sec. S7), we describe *ab initio* molecular dynamics simulations of Li nanoclusters in contact with and reacting with CF_x edges under short-circuit conditions. These are qualitative in nature, aimed to illustrate what can spontaneously occur under artificially accelerated conditions.

In this section we consider inserting one Li at a time, which is more relevant to slow discharge rate conditions seen in practical CF_x cells. Figure 3a depicts such a Li at the zigzag edge interface between CF and the defluorinated graphite region of partially defluorinated CF_x . The existence of sharp CF/C boundaries is motivated by our hypothesis that an edge-propagation mechanism would not significantly depend on F or Li-content (x in CF_x , Figure 1d) and to a lesser extent by

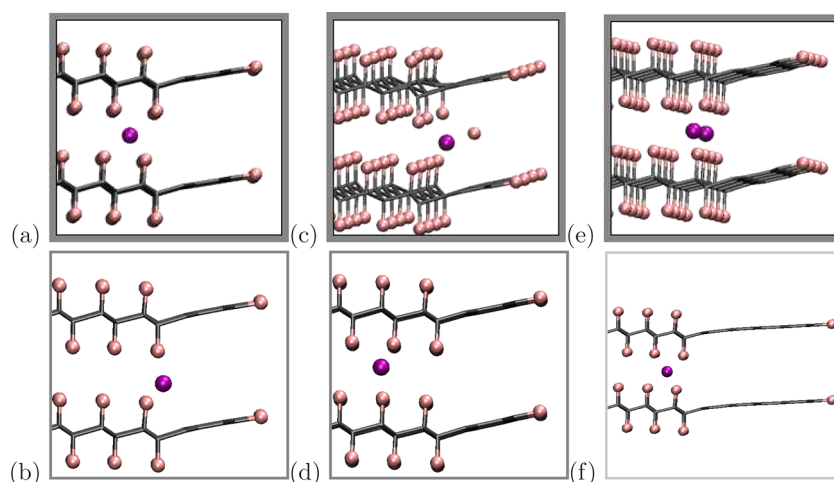


Figure 3. (a) 6-coordinated CF/C Li “interfacial site”. (b) 3-coordinated Li “outer binding site”. (c) Breaking a C–F bond in panel (b). (d) 6-coordinate Li-site inside the CF/C interface. (e) Inserting two Li at nearby CF/C interfacial sites. (f) CF/C interface site after further removal of several rows of F atoms from panel (a). For color key, see Figure 1.

AIMD simulation results (SI). At this “CF/C interfacial site”, Li is coordinated to six C–F groups.

Unlike the formation of LiF discharge products, which involves typically slower nucleation events, Li⁺ insertion into CF_x is diffusive, assisted by electric fields. It should be fast (Sec. III.A)³⁰ and reversible. This equilibrium assumption allows the use of

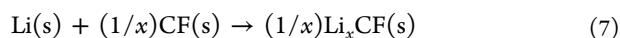
$$\text{el}\mathcal{V}_i = [E(\text{CFLi}_x) - E(\text{CFLi}_{x-\delta x})]/\delta x - E(\text{Li}) \quad (5)$$

to describe the observed voltage. Equation 5 would be identical to expressions used to calculate LiC₆ equilibrium voltages if “CF” is replaced with “C.” In this formulation, LiF(s) formation subsequent to Li insertion does not figure into \mathcal{V}_i , unlike in most previous DFT work. We find that Li insertion at the interfacial site (Figure 3a) yields $\mathcal{V}_i = 2.62$ V via eq 5. This value is in good agreement with the observed CF_x discharge plateau value of ~ 2.5 V (Figure 1a). GITT measurements, which should give voltages closer to equilibrium values, yield open circuit voltage values higher by only 0.4–0.5 V. This covers the \mathcal{V}_i range predicted. In the SI, we describe GITT analysis which shows that lithium diffusion rate in CF_x is reasonably fast.^{69,80}

This value of 2.62 V is surprising in light of the less favorable Li insertion into bulk CF; both fluorinated and defluorinated. Li⁺ intercalation into graphite (as model for defluorinated CF_x) has been extensively studied in the context of graphite anodes. The process is fast and reversible, even though an electron-insulating but ion-conducting solid electrolyte interphase film is present.^{38,71} This reaction,



occurs at $\mathcal{V}_i = 0.1$ –0.2 V vs Li⁺/Li(s), which is far lower than the observed CF_x discharge voltages (Figure 2). In contrast, the equilibrium voltages associated with Li-insertion into CF_x stacks (Figure 1a),



have not been reported. Our DFT/PBE calculations in the dilute limit ($x = 1/48$) yield 0.93 V vs Li⁺/Li(s). This \mathcal{V}_i is higher than that associated with LiC₆ but is significantly lower than experimental discharge voltages (Figure 2). Since the

excess e^- from Li insertion will reside in the conduction band of the insulating CF, the 0.93 V value is likely overestimated because the PBE functional underestimates band gaps. This value is consistent with the defect-free single CF sheet voltage of ~ 1.0 V reported in ref 54, after adjusting the Li atom binding energy used therein with the lithium metal cohesive energy reference.

The anomalously high \mathcal{V}_i at the interface compared to bulk phases is a manifestation of interfacial charge storage behavior.^{39,40} Li⁺ favors insertion into the CF region, where it is stabilized by CF polar groups, while the accompanying e^- is partially delocalized in the nearby metallic carbon region. This charge sharing principle is illustrated in the differential charge and spin density plot (Figure 4b), computed by

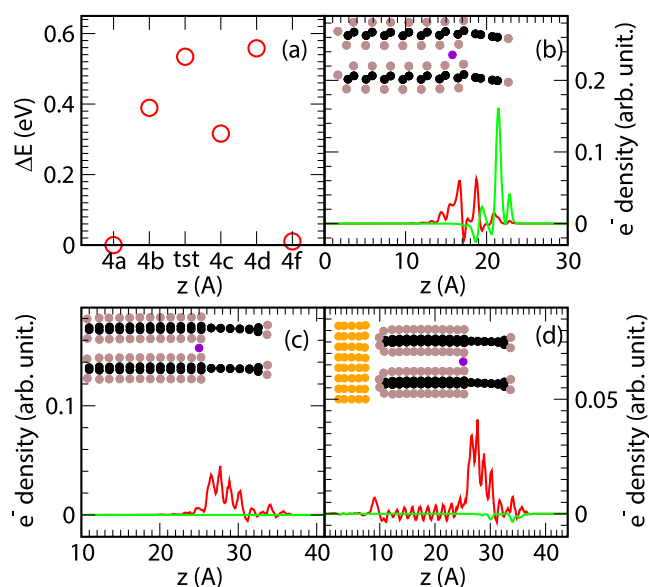


Figure 4. (a) Energy landscape for Figure 3 [recall panel (f) refers to a different F-content]. (b–d) Differential charge (red) and spin (green) densities before/after removing a Li atom. (b) Zigzag edge; the Li is at $z = 15.8$ Å. (c) Arm-chair CF/C interfaces; the Li is at $z = 15.2$ Å. (d) Same as (c) but with an Au(111) slab on the left side; Li is at $z = 25.2$ Å. For color key, see Figure 1.

removing the inserted Li atom while freezing all other atoms. In contrast, while graphite is metallic and readily accommodates an excess e^- , it interacts weakly with Li^+ , resulting in a low overall Li-binding energy and a low \mathcal{V}_i . For CF, the interaction between Li^+ and the polar C–F bond is more energetically favorable than that between Li^+ and graphite. However, CF_x is an insulator at large x , and adding e^- to its conduction band is unfavorable. Hence the interface between CF and defluorinated CF regions is uniquely suited to inserting Li.

III.D. Subsequent C–F Bond-Breaking Kinetics. Next we consider the steps subsequent to Li insertion. We move the inserted Li to a 3-coordinated surface site outside the interfacial site and reoptimize the configuration (Figure 3b). This will be referred to as the “outer binding site.” The energy associated with this site is a modest 0.39 eV higher than the interfacial site (Figure 3a). The subsequent C–F bond breaking event (Figure 3c), a prerequisite to LiF crystal formation, is exothermic by 0.07 eV relative to Figure 3b. It is endothermic relative to Figure 3a by 0.32 eV, but that enthalpy cost is compensated by the canonical ~ 0.4 eV entropy gained by releasing a “molecule” (LiF) at $T = 300$ K, due to the transformation of low-entropy vibrational degrees of freedom in a configuration with an intact C–F bond to the high-entropy rotational and translational degrees of freedom after the bond is broken.⁷² The value of ~ 0.4 eV assumes that the system is at equilibrium and the product is at a 1.0 M concentration in the liquid phase. In reality, the LiF product is continuously consumed and removed from the electrolyte, so 0.4 eV is a lower-bound rough estimate (SI section S6). The activation energy (ΔE^*) associated with this defluorination step is a modest 0.53 eV relative to Figure 3a. Assuming a standard kinetic prefactor of 10^{12} /s, once Li is inserted, F^- will be released in millisecond time scales at $T = 300$ K.

Over time, the released LiF diatomic fragment is expected to nucleate with other LiF units to form LiF nanocrystalline discharge products. These crystallites have been reported to be >10 nm in size²⁶ bulk-like for the purpose of calculating energetics, though more rigorous experimentation is needed to conclusively determine the final LiF dimensions in discharged CF_x cathode. Our DFT/PBE calculations show that $\text{LiF}(\text{g}) \rightarrow \text{LiF}(\text{s})$, where “(g)” and “(s)” stands for gas and crystalline solid phases respectively, is exothermic by 2.66 eV. Therefore LiF nanocrystal formation is not reversible unless >2.66 eV external energy is injected, for example, via applying a high potential (section III.G). This may help explain why Li/ CF_x cells have so far been nonrechargeable. We have not considered the kinetics or possible overpotentials associated with the subsequent nucleation or growth of LiF crystals from these 2-atom LiF units. However, a reactive molecular dynamics (MD) approach has previously shown that such growth can occur in MD time scales ($\ll 1$ s), in a different battery system.⁷³

III.E. Detailed Analysis of Li Insertion, Solvent Effects. Figure 3d depicts Li insertion further inside the CF region, away from the interface. It is unfavorable in energy by 0.56 eV relative to the interfacial site (Figure 3a), likely due to larger charge separation between the Li^+ and the partially delocalized injected e^- . Thus interior CF sites would not be occupied by Li unless the discharge occurs at significant overpotentials. Thus our proposed interfacial discharge intermediate phase is small in length scale and may be difficult to detect experimentally. The F-removal energy landscape with this zigzag edge is

depicted in Figure 4a. Far from the interface, Li insertion into CF should revert to the $\mathcal{V}_i = 0.93$ V reported in section III.C.

Figure 3e depicts adding a second Li atom at an interfacial site near the first. The energy gain in this step corresponds to $\mathcal{V}_i = 1.45$ V, which is significantly less favorable than the 2.62 V associated with the first Li. This finding suggests that the interfacial site is not saturated with Li. However, doubling the simulation cell y -dimension (Table 2, lines 6–7, not shown in figures) is found to reduce \mathcal{V}_i by only 0.01 V, suggesting that separation by ~ 1 nm is the saturation limit for interfacial Li atoms.

After removing one F-atom from Figure 3a, the next discharge event associated with the next Li insertion is 2.72 V (not shown), slightly higher than the 2.62 V before removing that F-atom. The C–F bond cleavage subsequent to this second Li-insertion is also energetically more favorable than before (-0.27 eV compared with $+0.32$ eV), and the activation energy is lower ($+0.32$ eV compared with 0.53 eV). The more favorable defluorination energetics is partly a manifestation of an “odd–even” electron spin effect discussed in the SI (section S3). Finally, we consider Li insertion at the interfacial site after a more substantial defluorination. Removing several rows of F atoms to leave another clean-cut CF/C boundary (Figure 3f) yields Li intercalation $\mathcal{V}_i = 2.56$ V at the interfacial site, which is only slightly less than the 2.62 V associated with Figure 3a. This conforms with the Figure 1d hypothesis that the defluorination voltage depends on the local environment, not the global F-content in CF_x . If the F-removal leaves a jagged boundary between the CF and C regions (not shown), \mathcal{V}_i is slightly increased, to 3.12–3.15 V depending on the defluorination extent. We note that row-by-row C–F bond breaking during discharge is limited by the “gatekeeper” site with the lowest local \mathcal{V}_i , which is in the 2.56–2.62 V range. At or below such voltages, a new intact row of CF groups can be defluorinated.

So far we have not addressed solvent effects. Figure 5a and b depict the addition of a single ethylene carbonate (EC) or fluoromethane (FM) solvent molecule to the Li at the 3-coordinated outer binding site (Figure 3b); they dovetail with eq 2 proposed in the literature.³⁰ EC is a standard battery electrolyte solvent molecule, similar in structure to PC used in Figure 2a and b; the discharge profile using EC (Figure 2c) is similar to that without EC. FM (featured in Figure 2d) is a key component of a recently proposed liquefied gas electrolyte particularly useful at low temperatures.^{13,14} In Figure 2, PC-based and EC-based electrolytes are found to exhibit discharge plateaus higher in voltage than FM-based electrolyte by 0.1–0.3 V. Our DFT predictions are that \mathcal{V}_i is higher for EC than FM, by 2.90 V vs 2.49 V (Figure 3a and b). This difference is only slightly higher than the experimental difference, but it is significantly less than the relative gas phase binding energy; we find that an EC binds to a single Li^+ more favorably than FM to Li^+ , by 1.09 eV. Figure 5c–f deals with isolated CF_x sheets rather than stacks. They are relevant to the exposed outer basal plane surfaces of CF_x stacks and large curvature, fluorinated nanotubes.²⁴ In these cases, no 6-coordinated Li^+ binding site exists between two CF_x sheets, and solvent molecules may be necessary to stabilize Li adsorption. Here we postulate that isolated CF_x sheets also undergo row-by-row defluorination and exhibit sharp interfaces between CF and C regions. In Figure 5d, we place a Li at the surface site coordinated to 3 CF bonds and an EC molecule on the zigzag edge. After

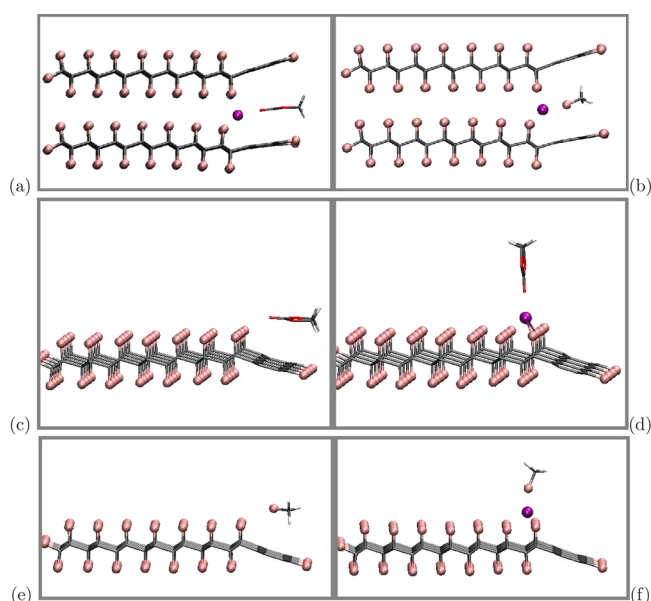


Figure 5. (a–b) Adding a single EC or FM solvent molecule to Li^+ at the 3-coordinated outer binding site at the zigzag edge. (c) EC on isolated partially defluorinated CF_x sheet. (d) Same as (c) but with Li^+ coordinated to 3 CF bonds and the EC molecule. (e) FM on isolated partially defluorinated CF_x sheet. (f) Same as (e) but with Li^+ coordinated to 3 CF bonds and the FM molecule. The \mathcal{V}_i values associated with panels (a), (b), (d), and (f) are 2.90, 2.49, 2.66, and 2.25 V, respectively. The color key is as in Figure 1; in addition red and white sticks represent O and H atoms.

optimizing atomic positions, the Li^+ becomes strongly coordinated to two CF groups and less strongly bound to a third CF (Figure 5d). \mathcal{V}_i for this configuration is 2.66 V, less than the 2.90 V for Figure 5a but still in reasonable agreement with experimental measurements (Figure 2). This suggests that our Li^+ intercalation mechanism applies to isolated CF_x sheets, not just stacks. The corresponding value for FM (Figure 5f) is 2.25 V, less than the 2.49 V for Figure 5b.

The \mathcal{V}_i variation due to EC or FM coordination is 0.41–0.42 V, qualitatively similar to those found in our experimental measurements (Figure 2), further supporting our computational interpretation of CF_x discharge behavior. These \mathcal{V}_i are also within a few tenths of a volt of the solvent-free 2.62 V at the 6-coordinated interfacial site at this F-content (Figure 3a); they remain far closer to experimental discharge voltages than previous DFT calculations.

We caution that these equilibrium voltages are calculated using a gas phase solvent molecule reference. They ignore solvent–solvent attractive free energies which may add 0.3–0.5 eV to the cost of each solvent molecule. It is difficult to estimate the EC or FM desolvation free energy contribution because the electrolytes have mixed solvents and salts, the DFT/PBE method underestimates dispersion forces between solvent molecules and between solvent molecules and graphite sheets, and the entropy contributions involved are difficult to estimate. However, in the Figure 5d and f configurations, if a liquid solvent were in the simulation cell, the EC or FM coordinated to Li^+ would have been partially surrounded by solvent molecules. So these configurations would exhibit far less desolvation corrections than Figure 5a and b, where embedding EC and FM between graphite sheets would hinder them from interacting with other solvent molecules. Despite

this difference, the $\Delta\mathcal{V}_i$ predicted when using EC (Figure 5d) and FM (Figure 5f) molecules is almost the same as that associated with Figure 5a and b. This strongly suggests that bulk liquid effects do not strongly modify our conclusion about solvent differences predicted in vacuum.

We stress that the true \mathcal{V}_i in any electrolyte is bounded from below by the solvent-free value. If solvent-coordinated Li^+ at the outer binding site is not more favorable than the solvent-free interfacial site (Figure 3a), the solvent will not contribute to \mathcal{V}_i . This helps explain the limited electrolyte-dependence observed during Li/ CF_x discharge (Figure 2 and refs 10–12), compared to the much larger dependence of gas phase binding energies on solvent molecules. Note also that we choose the solvent models here to compare with our measurements. In the future, we will consider solvents found in commercial Li/ CF_x cells like γ -butyrolactone.⁷⁴

III.F. Arm-Chair Edges. As discussed in the SI (section S4), arm-chair edge CF_x partially defluorinated in the direction normal to the edge yields insulating carbon because of tensile strain. If the periodic boundary condition is removed in the lateral direction so the model represents a finite sheet, this carbon will likely spontaneously develop a curvature, reducing the strain and the electronic band gap. However, the CF_x/C interface region may still exhibit local strain, which may be measurable in Raman spectroscopy.^{75,76} In this work, we focus on periodically replicated arm-chair edges.

Figure 6a depicts the insertion of a Li atom into the arm-chair interfacial site, which is coordinated to 4 C–F groups. In

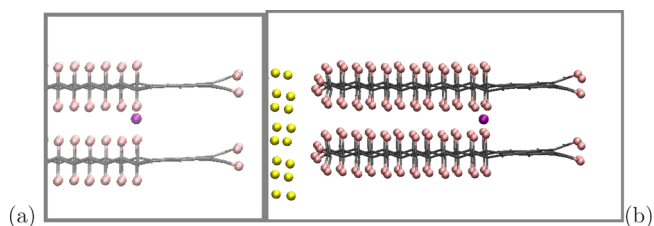


Figure 6. (a–b) Li-insertion at arm-chair edge CF/C interfaces, with and without an Au current collector (yellow).

this configuration, \mathcal{V}_i is 1.49 V, lower than the zigzag edge value. This is consistent with the fact that it now costs extra energy to deposit an e^- into the conduction band of the system because of the finite band gap (SI section S4). Charge density changes induced by Li-insertion (Figure 4c) show that the excess e^- still causes somewhat localized changes at the interface, but over a larger graphite region than zigzag.

In a working battery cathode, metallic electrode behavior is maintained by adding conductive carbon additives and depositing the material onto a current conductor. CF_x is also converted to conductive carbon upon discharge. In Figure 6b, we add a Au(100) current collector to the system to qualitatively mimic an electronically conducting component. \mathcal{V}_i is predicted to be 1.81 V, which is 0.32 V more favorable than the model without Au (Figure 6a) but is still significantly lower than the zigzag value of 2.62 V, or experimental discharge voltages (Figure 2). Therefore an external current collector does not strongly alter the equilibrium voltage associated with Li insertion. The excess density plot (Figure 4d) shows significant delocalization of excess e^- over the CF region, but little of the excess charge is on the Au electrode, likely because the metallic region is too far from the interface

to yield benefits. We conclude that CF/C interfaces at zigzag edges are more active than those at arm-chair edges in terms of CF_x discharge. In the SI (section S5), we consider electronic voltage effects in this system.⁶⁵

We have also examined the outer binding site with Li^+ coordinated to 3 C–F bonds and an EC molecule (not shown but analogous to Figure 5a). \mathcal{V}_i is 1.96 V in this case, substantially lower than either measurement with carbonate electrolytes (Figure 2a and c) or the 2.92 V zigzag edge value. These calculations demonstrate the importance of a metallic carbon region in CF_x discharge.

In the SI, we also compare insertion of Na rather than Li into CF_x (section S8). The predicted voltages are found to be similar but the C–F bond-breaking event exhibits a larger barrier and is slower. We speculate that multiple Na^+ coordinated to one C–F group may reduce the C–F bond-breaking barrier there and play a role in Na/ CF_x discharge.

III.G. Recharge Calculations. In this section, we return to the Li/ CF_x zigzag edge model (Figure 3a) and consider Li/ CF_x recharge. We add a LiF slab outside the partially defluorinated CF_x edge (Figure 7a, Table 1). The slab is

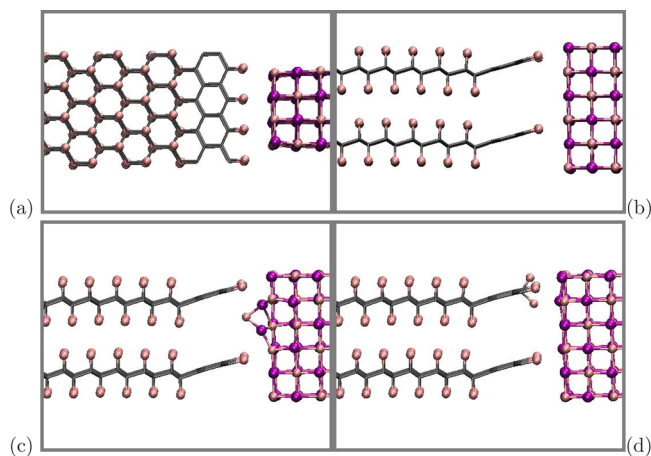


Figure 7. (a–b) Two views of the finite LiF slab at the zigzag surface of the CF_x/C interface; (c) F^- moved to the inner surface; (d) formation of a C–F bond. LiF is three bilayers (~ 12 Å) thick in the z direction (left-to-right).

periodically replicated in the direction perpendicular to the CF_x sheets but is finite in extent in the other lateral direction (Figure 7a and b). This baseline model system mimics discharged LiF residing on the defluorinated CF_x edge.

Next, a F^- anion is moved from the outer LiF surface to its inner surface closest to the CF_x edge, where it is now coordinated to two Li^+ ions (Figure 7c). This configuration mimics voltage-driven F^- diffusion through the LiF discharge product toward the defluorinated carbon, where it ultimately reconstitutes a C–F bond. The energy cost associated with creating the defect (Figure 7c) from the defect-free sheet (Figure 7a and b) is 2.44 eV in this $12.2 \times 10.4 \times 44.0$ Å³ simulation cell. This periodically replicated cell is charge neutral but exhibits a significant dipole moment which can lead to electrostatic energy artifacts.⁷⁸ Using larger, $1 \times 2 \times 1$ and $2 \times 2 \times 1$ surface supercells, the energy costs are $\Delta E = 2.14$ and 2.21 eV, respectively, suggesting that this energy has converged to within ~ 0.1 eV. During recharge, this energy cost needs to be provided by changing the applied electronic voltage \mathcal{V}_e .⁶⁵ A more complete discussion of \mathcal{V}_e is given in the

SI (section S5). Figure 7d depicts a configuration where the F^- on the inner LiF surface is further transferred to the carbon region to form a C–F bond. $\Delta E = -0.26$ eV relative to Figure 7c, and the barrier is a small $\Delta E^* = 0.19$ eV. This suggests that reformation of C–F bonds from nearby undercoordinated F^- anions can readily occur; formation of this bond is not the prohibitive rate-limiting step.

To show that a voltage change can cause F^- diffusion from the LiF outer surface to its inner surface prior to C–F bond formation, we create an artificial electric field by removing a Li^+ from the outer interface of the LiF slab. In terms of electronic voltage,⁶⁵ the Li^+ vacancy causes the Figure 7a and b \mathcal{V}_e to increase from 4.02 to 6.46 V. This latter \mathcal{V}_e is artificially high, partly because of the lack of a liquid electrolyte beyond the outside surface of the LiF slab. However, \mathcal{V}_e includes contributions from many interfaces, including the LiF/vacuum and C/LiF interfaces which should be similar before and after Li^+ vacancy formation. It is the electric field across the LiF slab, reflected in the voltage difference between the two cases ($\Delta\mathcal{V}_e = +2.44$ V), that is relevant to our calculation.

Upon creating the Li^+ vacancy on the outer LiF surface, the Figure 7c configuration is no longer metastable, unlike the case without the Li^+ vacancy. The ΔE for moving a F^- from the outer LiF surface (Figure 7d) to the inner surface and reforming a C–F bond decreases from an endothermic +2.19 eV to an exothermic (favorable) -0.93 eV in the $1 \times 1 \times 1$ surface cell. The corresponding ΔE for the $2 \times 2 \times 1$ surface cell is even more favorable at -1.45 eV. These ΔE 's strongly suggest that refluorination and recharging are energetically and kinetically viable near the outer defluorinated CF_x surface in contact with LiF discharge products if a sufficient electric field is applied.

Note that we have focused on reforming a C–F bond at the outer defluorinated CF_x surface, not the CF_x/C interface which is the focus of the discharge calculations (Figure 3). Therefore we assume recharge occurs “from outside in”. The reason is that we assume F^- anions are poorly solvated by organic solvent molecules. This suggests that moving F^- to the CF_x/C interface may entail a large barrier. (In contrast, Li^+ is much better solvated by organic solvents and can be readily transported to the CF_x/C interface via $\text{Li}^+(\text{solvent molecule})_n$ complexes and can initiate discharge there.) If this hypothesis is correct, CF_x charge and discharge will follow different pathways. This may be an important consideration when designing practical rechargeable Li/ CF_x cathodes.

IV. CONCLUSIONS

The existence of a CF_x discharge “intermediate phase” has been proposed in the literature to explain the discharge behavior of Li/ CF_x batteries, but its identity has so far not been elucidated. In this work, we hypothesize an intermediate phase associated with a CF_x edge-propagation Li-insertion mechanism. Our DFT calculations show that Li intercalation at the zigzag edge boundary between fluorinated (i.e., CF) and defluorinated (carbon) regions exhibits an equilibrium voltage about 2.6 V vs $\text{Li}^+/\text{Li}(s)$. The predicted voltage range is in good agreement with experimental CF_x electrochemical discharge voltage profiles and is only 0.4–0.5 V lower than GITT measurements. Li-insertion is favorable there because of partial separation of Li^+ and e^- charges at the interface, in accordance with the “interfacial charge storage” paradigm.³⁹ Na/ CF_x is predicted to exhibit similar discharge voltages (SI).

Our proposed CF_x intermediate phase has a spatial extent limited to the CF/C interface thickness. These predictions should assist a renewed experimental attempt to locate the CF_x intermediate phase. Our predicted voltages do not involve C–F bond breaking or LiF nucleation energetics.

This proposed mechanism is not inconsistent with the existence of a thin, several-atom-thick LiF layer that may reside between CF_x sheets, swelling the cathode material in the process. Indeed, our hypothesis may provide a viable pathway to realize a $\text{CF}_x\cdot\text{Li}_y$ intermediate phase. We also show that post Li-insertion CF_x discharge kinetics, especially C–F bond breaking, are sufficiently fast in Li/ CF_x batteries when a C–F bond is polarized by the inserted Li^+ cation nearby. The proposed discharge mechanism helps explain why solvent dependence on discharge voltage should be small. Our predicted variation in voltage plateau values as the electrolyte varies is in qualitative agreement with our discharge measurements in organic carbonate and liquified gas electrolytes. Finally, we propose that Li/ CF_x recharge may proceed via a pathway distinct from the one encountered during discharge.

Our computational work does not invoke phase diagram calculations and therefore does not assume that CF_x and LiF are in equilibrium. Since Li/ CF_x batteries are not rechargeable so far, the equilibrium assumption appears untenable. Thus our work provides a novel, general framework for understanding and modeling the discharge behavior of new types of primary batteries. For example, in recent work on SF_6 -based primary batteries, the equilibrium assumption underlying the traditional phase diagram approach also seems inapplicable.⁷⁷ For future work, electric field and electronic voltage effects need to be addressed more explicitly by including liquid electrolytes in more rigorous AIMD simulations. Straining effects and CF_x heterogeneity^{41–43} will also be considered to further improve our discharge voltage predictions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c04676>.

Experimental details; F-vacancy diffusion barriers in CF_x ; odd–even energetic effects on defluorination; local electronic densities of state; electronic voltage discussions; entropy considerations; short-circuit AIMD simulations; Na/ CF_x predictions (PDF)

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Notes

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