

# Revisiting the conversion reaction voltage and the reversibility of the CuF<sub>2</sub> electrode in Li-ion batteries

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## ABSTRACT

Deviation between thermodynamic and experimental voltages is one of the key issues in Li-ion conversion-type electrode materials; the factor that affects this phenomenon has not been understood well in spite of its importance. In this work, we combine first principles calculations and electrochemical experiments with characterization tools to probe the conversion reaction voltage of transition metal difluorides MF<sub>2</sub> (M = Fe, Ni, and Cu). We find that the conversion reaction voltage is heavily dependent on the size of the metal nanoparticles generated. The surface energy of metal nanoparticles appears to penalize the reaction energy, which results in a lower voltage compared to the thermodynamic voltage of a bulk-phase reaction. Furthermore, we develop a reversible CuF<sub>2</sub> electrode coated with NiO. Electron energy loss spectroscopy (EELS) elemental maps demonstrate that the lithiation process mostly occurs in the area of high NiO content. This suggests that NiO can be considered a suitable artificial solid electrolyte interphase that prevents direct contact between Cu nanoparticles and the electrolyte. Thus, it alleviates Cu dissolution into the electrolyte and improves the reversibility of CuF<sub>2</sub>.

## 1 Introduction

Lithium-ion batteries have been used as energy sources in various mobile and stationary applications. In order to meet the growing demand for mass-market adoption, substantial improvement in energy density and reduction in the cost of rechargeable batteries are

crucial [1]. Conversion materials have a higher Li-storage capacity than commercialized intercalation electrode compounds [2]. Among conversion materials, transition metal difluorides MF<sub>2</sub> (M = Fe, Ni, Cu), especially show a relatively higher reaction voltage due to the strong M–F ionic bond [3]. In order to achieve the potential implication of these compounds

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in rechargeable batteries, wide progress has been made. Badway et al. developed a carbon-metal fluoride nanocomposite composed of nano-domains of  $\text{FeF}_3$  with a high surface-to-volume ratio in a carbon matrix. It was demonstrated that the high surface-to-volume ratio of nano-sized  $\text{FeF}_3$  are electroactively improved [4, 5]. Later, they introduced another concept of nanocomposite design that enables  $\text{CuF}_2$  to have 98% of the theoretical discharge capacity within the voltage range 2.0–4.0 V vs.  $\text{Li}/\text{Li}^+$ . The nanocomposite composed of a carbon matrix with intercalation compounds (e.g.,  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{MnS}_2$ ) promoted electron and ion conductivity [6]. Oxygen doping into metal fluorides, such as  $\text{FeOF}$  and  $\text{Fe}_2\text{OF}_4$ , has also been shown to enhance electrochemical properties [7–10]. It is proposed that the substitution of O for F increases the average conversion voltage and facilitates cycling stability by incorporating more covalent M–O bonds into the ionic fluoride structure. Recently, Wang et al. reported reversible binary metal fluorides  $\text{Cu}_y\text{Fe}_{1-y}\text{F}_2$  [11]. They proposed the incorporation of Cu into the  $\text{FeF}_2$  crystal lattice, which promotes the reversible redox behavior  $\text{Cu}^{2+} \leftrightarrow \text{Cu}^0$ . Even though the reversible capacity of Cu content degrades due to dissolution of Cu, the binary fluoride exhibits low hysteresis with high voltage and capacity.

Despite progresses in conversion materials as promising materials for future batteries, there are still unsolved issues: (i) the discrepancy between the experimental voltage of transition metal difluorides,  $\text{MF}_2$ (M = Fe, Ni, Cu) and the theoretical thermodynamic voltage, and (ii) the non-reversible conversion reaction of  $\text{CuF}_2$ . As for the voltage discrepancy, it has been reported that the experimental voltage plateau for  $\text{MF}_2$ (M = Fe, Ni, Cu) is lower than the thermodynamic reaction voltage [12, 13]. In order to understand the origin of the voltage deviation, we used density functional theory (DFT) and calculated the conversion reaction voltage depending on the size of the M(M = Fe, Ni, Cu) nanoparticle formed during discharge. We also conducted a PITT experiment on  $\text{NiF}_2$  and  $\text{CuF}_2$  electrodes to observe near-equilibrium conversion reaction voltages. The average sizes of Ni and Cu nanoparticles during lithiation were measured by scanning transmission electron microscopy (STEM) to correlate the nano-size effect of metal particle

formation with the reaction voltages.

The  $\text{CuF}_2$  electrode has the highest theoretical voltage among  $\text{MF}_2$ (M = Fe, Ni, Cu) species, which is suitable for power-driven mobile devices; however,  $\text{CuF}_2$  is intrinsically non-reversible in contrast to  $\text{FeF}_2$  and  $\text{NiF}_2$  [14, 15]. Wang et al. reported that the origin of irreversibility is due to the separation between relatively large Cu nanoparticles (5–12 nm in diameter) and LiF, which blocks electron paths [14]. Yamakawa et al. suggested that the different diffusivities of the ionic phases ( $\text{F}^-$  and  $\text{Li}^+$ ) bring about the formation of an LiF coating on the  $\text{CuF}_2/\text{Cu}$  and  $\text{CuF}_2/\text{electrolyte}$  interfaces and hinders the reversible reaction [16]. Recently, Hua et al. reported that the degradation mechanism of  $\text{CuF}_2$  is associated with Cu dissolution along with LiF consumption [17]. In this study, we apply a NiO coating on  $\text{CuF}_2$  to study the effect of NiO on the reversible  $\text{CuF}_2$  conversion reaction. As NiO is not electrochemically active within our voltage range (2.0–4.0 V), it does not contribute additional capacity to  $\text{CuF}_2$ . This is opposed to the cases of other metal oxides such as  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{MnS}_2$  that have been adopted to the  $\text{CuF}_2$  conversion reaction [6]. ADF-STEM and electron energy loss spectroscopy (EELS) were used to suggest a reversible conversion mechanism for the NiO-coated  $\text{CuF}_2$  electrode.

## 2 Experimental

### 2.1 Computational methodology

We conducted first principles calculations [18] based on spin-polarized GGA and GGA +  $U$  [19, 20] using the Perdew–Burke–Ernzerhof exchange and correlation functionals [21]. We used a plane-wave basis set and the projector-augmented wave (PAW) method [22, 23] as parameterized in the Vienna *ab initio* simulation package (VASP) [24]. A gamma point mesh is performed with  $9 \times 7 \times 7$   $k$ -points for  $\text{CuF}_2$ ,  $7 \times 7 \times 11$   $k$ -points for  $\text{NiF}_2$ , and  $7 \times 7 \times 9$   $k$ -points for  $\text{FeF}_2$ . For metal nanoparticles, gamma point was used to sample the Brillouin zone, and periodic boundary conditions were imposed on the unit cell where vacuum size was larger than the nanoparticle diameter to prohibit interactions between the images. All the atoms were fully relaxed to calculate the optimized structure



with a cutoff energy of 1.3 times the maximum cutoff specified by the pseudopotentials on a plane wave basis set. Our GGA +  $U$  calculations indicate that the lattice parameters of metal fluorides agreed well with experimental measurements and the error is less than 2% (Table S1 in the Electronic Supplementary Material (ESM)). It is noted that we adopted a mixed GGA and GGA +  $U$  framework as proposed by Jain et al. [25] in order to obtain accurate reaction energy and voltage of conversion reaction. The detailed explanation of the framework is discussed in the results and discussion section.

## 2.2 Material preparation

Commercial CuF<sub>2</sub> (Aldrich) and NiF<sub>2</sub> (Alfa Aesar) powders were used for this study. In order to synthesize carbon coated with metal difluoride, CuF<sub>2</sub>/C (or NiF<sub>2</sub>/C), we prepared a milling jar where 80 wt.% of conversion material and 20 wt.% of acetylene black (Strem Chemicals) were mixed together in an MBraun Ar-filled glovebox (H<sub>2</sub>O < 0.1 ppm). The jar was sealed with Parafilm before being transferred to a planetary ball mill (PM 100, Retsch) and the milling was performed for 6 hours at 500 rpm. In addition, NiO (Aldrich) coated CuF<sub>2</sub> (NiO-CuF<sub>2</sub>) with the composition CuF<sub>2</sub>:NiO = 85:15 w/w was prepared by ball milling for 4 hours at 650 rpm under an Ar atmosphere. NiO-CuF<sub>2</sub> was milled again with acetylene black to synthesize carbon-coated samples (NiO-CuF<sub>2</sub>/C). The mass loadings of CuF<sub>2</sub> and NiF<sub>2</sub> in the PITT discharge experiment were 1.36 and 1.49 mg·cm<sup>-2</sup>, respectively. Considering the cycling test of CuF<sub>2</sub> and NiO-CuF<sub>2</sub>, 0.84 and 1.17 mg·cm<sup>-2</sup> of CuF<sub>2</sub> were used.

## 2.3 Material characterizations

The electrochemical cells were disassembled in an argon-filled glovebox, and the electrodes were washed with dimethylene carbonate (DMC). The electrodes were scraped to produce a fine powder. A small amount of powder was placed on a transmission electron microscopy (TEM) lacy carbon film supported on a copper grid. Selected area electron diffraction (SAED) patterns, ADF-STEM images, and EELS were acquired using a JEOL 2010F operated at 197 kV and equipped with a Gatan GIF 200 spectrometer. The EELS spectra

were obtained with a collection half angle of 27 mrad and convergence angle of 10 mrad (with an energy resolution of 0.9 eV). Additionally, the ADF-STEM image as an EELS spectrum image was attained using a TEAM 0.5 aberration-corrected instrument operating at 80 kV at Lawrence Berkeley National Laboratory, equipped with a high brightness Schottky-field emission electron source. The ADF-STEM image and EELS elemental maps were acquired using a Gatan Efinia spectrometer with a collection angle of 52 mrad and convergence angle of 30 mrad. Cu dissolution into the electrolyte was characterized by inductively coupled plasma optical emission spectroscopy (ICP-OES) (PerkinElmer Plasma 3700). The electrolyte (25  $\mu$ L) was gathered from a custom-made electrochemical cell and included into a 25 mL solution matrix (1:1 w/w, HNO<sub>3</sub>/HCl). Therefore, the electrolyte was examined at a 1,000-fold dilution [26].

## 2.4 Electrochemical characterization

Electrochemical characterization was performed using coin-type (2016) cells. We used a battery cycler (Arbin) at room temperature. We made working electrodes composed of active materials (NiO-CuF<sub>2</sub>/C, CuF<sub>2</sub>/C or NiF<sub>2</sub>/C), acetylene black, and polyvinylidene fluoride (PVDF) with a 70:20:10 w/w ratio. Pure lithium metal was used as counter electrode and polypropylene C480 (Celgard) was used as the separator. The coin cells were assembled with the electrolyte consisting of 1 M LiPF<sub>6</sub> dissolved in EC and DMC at a weight ratio of 1:1 (BASF) in an MBraun Ar-filled glovebox (H<sub>2</sub>O < 0.1 ppm). The theoretical specific capacities of CuF<sub>2</sub> and NiF<sub>2</sub> are 528 and 554 mAh·g<sup>-1</sup>, respectively, which are used to set the C rate. PITT was adopted on the first discharge of CuF<sub>2</sub>/C and NiF<sub>2</sub>/C cells with the voltage limits of 2.0 and 1.0 V, respectively. The voltage step size was 10 mV with a cut-off current density of C/1,000 of active material. In addition, electrochemical cycling of NiO-CuF<sub>2</sub>/C and CuF<sub>2</sub>/C were tested with the constant current density of C/35. The cell voltage range of 2.0–4.0 V was applied. The first discharge of CuF<sub>2</sub>/C and NiF<sub>2</sub>/C were performed with the constant current density of C/35, and the discharge voltage limit of 2.0 and 1.0 V, respectively. For the linear potential sweep voltammogram, Cu

foil was employed as the working electrode. Other conditions including a coin-type cell, a separator, electrolyte, and a reference electrode were the same as the battery experiments. The scan rate was  $1 \text{ mV}\cdot\text{s}^{-1}$ .

### 3 Results and discussion

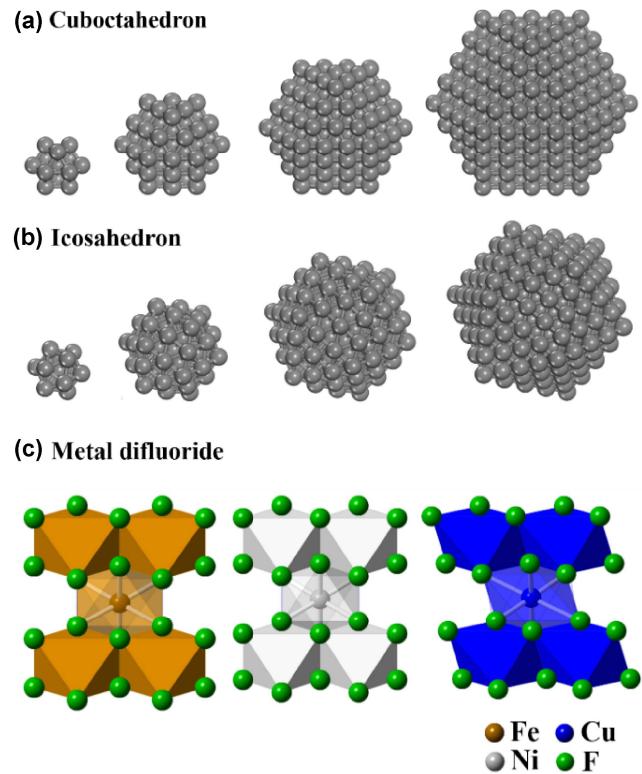
#### 3.1 Computational model systems

We set up four different sizes of metal nanoparticle models,  $M_n^{\text{cubo or icosa}}$  ( $n$  is the number of atoms in the nanoparticle), as shown in Figs. 1(a) and 1(b), in order to calculate the conversion voltage of  $\text{MF}_2$  ( $\text{M} = \text{Fe}, \text{Ni}, \text{Cu}$ ), with respect to the metal nanoparticle size

- (i)  $M_{13}^{\text{cubo or icosa}}$  (13 atoms and  $\sim 0.5 \text{ nm}$  in diameter),
- (ii)  $M_{55}^{\text{cubo or icosa}}$  (55 atoms and  $0.9\text{--}1.0 \text{ nm}$  in diameter),
- (iii)  $M_{147}^{\text{cubo or icosa}}$  (147 atoms and  $1.4\text{--}1.5 \text{ nm}$  in diameter), and
- (iv)  $M_{309}^{\text{cubo or icosa}}$  (309 atoms and  $1.9\text{--}2.0 \text{ nm}$  in diameter).

The average distance between two diametrically opposed vertices is defined to be the size of a nanoparticle and its radius is listed in Table S2 in the ESM. The shapes of the nanoparticles are ideal cuboctahedron and icosahedron structures, solely consisting of (111) and (100) planes [27], and a (111) plane [28], respectively. These planes correspond to the low Miller index planes with low surface energies [29] resulting in an optimal configuration (cuboctahedron and icosahedron) with minimal total free energy for a given particle size [30–33]. These morphologies are quite similar to the “magic number” nanoparticles, which also have been found to be thermodynamically stable [27, 34]. Because the activation energy to transform morphology among ultra-small nanoparticles is very small [35, 36], our model structures can be converted to different structures. This effect is outside the scope of the present study.

The metal difluorides investigated in our study are  $\text{FeF}_2$ ,  $\text{NiF}_2$ , and  $\text{CuF}_2$  (Fig. 1(c)). These crystals have rutile-type structure where the transition metal atoms are surrounded by 6 fluorine atoms.  $\text{CuF}_2$  crystallizes in the monoclinic structure ( $\text{P } 1 \text{ } 21/n \text{ } 1$  space group) that produces a highly distorted octahedron.  $\text{NiF}_2$  and  $\text{FeF}_2$ , however, have a tetragonal structure with  $\text{P } 42/m \text{ n } \text{m}$  space group.



**Figure 1** Model systems of (a) cuboctahedron and (b) icosahedron for Fe, Ni, and Cu, composed of 13, 55, 147, and 309 atoms (Fe cuboctahedron: 0.5, 1.0, 1.4, and 2.0 nm in diameter; Fe icosahedron: 0.5, 1.0, 1.4, and 1.9 nm in diameter; Ni cuboctahedron: 0.5, 1.0, 1.5, and 1.9 nm in diameter; Ni icosahedron: 0.5, 0.9, 1.4, and 1.9 nm in diameter; Cu cuboctahedron: 0.5, 1.0, 1.5, and 2.0 nm in diameter; Cu icosahedron: 0.5, 1.0, 1.5, and 1.9 nm in diameter). (c) The crystal structures of  $\text{FeF}_2$ ,  $\text{NiF}_2$ , and  $\text{CuF}_2$ .  $\text{FeF}_2$  and  $\text{NiF}_2$  are tetragonal, and  $\text{CuF}_2$  is the monoclinic.

#### 3.2 Influence of metal-nanoparticle size on the conversion reaction voltage

The electrochemical conversion of transition metal difluorides  $\text{MF}_2$  ( $\text{M} = \text{Fe}, \text{Ni}, \text{Cu}$ ) with Li is the two-electron reaction where the divalent metal ion is reduced to the metallic phase.



The thermodynamic voltage ( $E_{\text{thermodynamic}}^{\text{bulk}}$ ) for the reaction (Eq. (1)) can be obtained from [12]

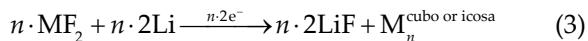
$$E_{\text{thermodynamic}}^{\text{bulk}} = \frac{G_f(2\text{LiF}) - G_f(\text{MF}_2)}{-2F} \quad (2)$$

where  $G_f$  and  $F$  are the standard Gibbs free energy of formation from thermodynamic tables and the Faraday



constant, respectively. It is noted that  $G_f$  relates to the bulk-phase formation energy so that  $E_{\text{thermodynamic}}^{\text{bulk}}$  acquired from  $G_f$  corresponds to the conversion voltage for the bulk-phase reaction. Most experimental reports on  $\text{MF}_2$  ( $\text{M} = \text{Fe}, \text{Ni}, \text{Cu}$ ) conversion reactions, however, show that the experimental voltage is much lower than  $E_{\text{thermodynamic}}^{\text{bulk}}$ , by up to ~1.5 V [6, 13–16, 37, 38]. Interestingly, the discharge reaction does not generate bulk-phase metal. It is reported that bulk  $\text{MF}_2$  is reduced to nanoscale M particles ( $\leq 10 \text{ nm}$ ) at the first discharge [14–16, 37, 38]. The origin of metal nanoparticle formation is estimated to be the tunneling of electrons from the carbon conductor to the inside of poorly conductive  $\text{MF}_2$  and forms M nanoparticles [16].

In order to understand the influence of metal nanoparticle formation on the conversion voltage using DFT, we replaced the bulk metal (M) in Eq. (1) with a metal nanoparticle composed of  $n$  atoms ( $\text{M}_n^{\text{cubo or icosa}}$ )



where  $\text{MF}_2$ , Li, and LiF are bulk-phase forms. Then, we adopted the framework of mixing GGA and GGA +  $U$  proposed by Jain et al. [25]. This method connects GGA and GGA +  $U$  energies, which are reasonable methods to calculate the ground state properties of materials for delocalized electronic states (e.g., metal and LiF) and localized electronic states of d orbitals (e.g., transition metal difluorides), respectively [39]. The computational cell voltage ( $E^{\text{nano}}$ ) is obtained as

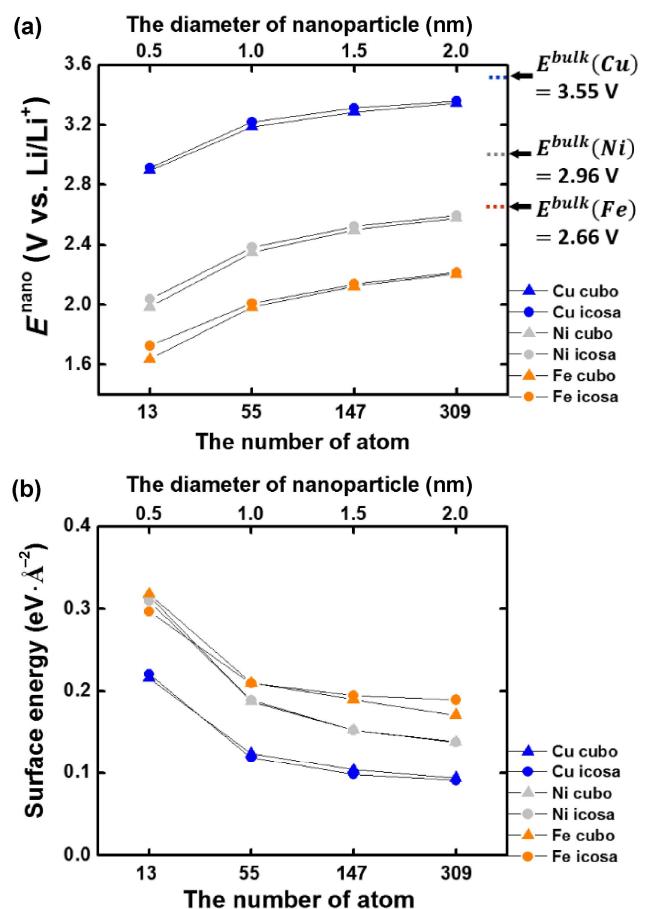
$$E^{\text{nano}} = \frac{\left[ n \cdot G^{\text{GGA}}(2\text{LiF}) + G^{\text{GGA}}(\text{M}_n^{\text{cubo or icosa}}) \right] - \left[ n \cdot G_{\text{renorm}}^{\text{GGA+U}}(\text{MF}_2) + n \cdot G^{\text{GGA}}(2\text{Li}) \right]}{-2n} \quad (4)$$

$G_{\text{renorm}}^{\text{GGA+U}}(\text{MF}_2)$  is calculated as  $G^{\text{GGA+U}}(\text{MF}_2) - \Delta E_{\text{M}} \cdot \Delta E_{\text{M}}$  connects GGA with GGA +  $U$  schemes and we adopted 1.723, 2.164, and 1.156 eV for Fe, Ni, and Cu (per atom), when  $U$  are 4.0, 6.0, and 4.0 for Fe, Ni, and Cu, respectively [25]. In order to confirm that the mixing framework is suitable for our calculations, we present the comparison of the bulk-phase reaction voltage (Table S3 in the ESM) measured from the GGA method, mixed GGA/GGA +  $U$  method, and the tabulated Gibbs free energy of formation [40]. The voltage from the mixed GGA/GGA +  $U$  method shows <0.09 V difference with respect to the voltage measured from

the thermodynamic table.

We find that  $E^{\text{nano}}$  for transition metal difluorides ( $\text{FeF}_2$ ,  $\text{NiF}_2$ , and  $\text{CuF}_2$ ) is lower than  $E_{\text{thermodynamic}}^{\text{bulk}}$  as shown in Fig. 2(a).

The voltage discrepancy between  $E^{\text{nano}}$  and  $E_{\text{thermodynamic}}^{\text{bulk}}$  is 0.19–1.02 V for metal nanoparticles sized  $\leq 2 \text{ nm}$ . This low voltage on formation of metal nanoparticles resembles the conversion voltage measured from experiments, which also exhibits a lower value than the thermodynamic voltage. Ko et al. displayed that the conversion voltage at the first discharge was evaluated to be 1.84 V which is lower than the thermodynamic voltage (2.66 V) on the lithiation reaction of  $\text{FeF}_2$  (very slow C rate, approximately  $C/1,000$ ) [13]. Another study using the



**Figure 2** (a) Calculated conversion reaction voltage as a function of the size of M nanoparticle ( $\text{M} = \text{Fe}, \text{Ni}$  and  $\text{Cu}$ ) formed. (b) Surface energy of M nanoparticle as a function of its size. The lower x-axis represents the number of atom contained in metal nanoparticle. The upper x-axis is the nanoparticle size in diameter which is approximate value. Detailed size information is demonstrated in Table S2 in the ESM.

galvanostatic intermittent titration technique (GITT) on the conversion reaction of  $\text{FeF}_3$  presented a voltage difference [41]. The second plateau (2.36 V) corresponds to the reduction of  $\text{Fe}^{2+}$  to Fe, which is lower than the thermodynamic voltage. The voltage discrepancy is also commonly found in transition metal oxide cathode materials while nanoscale metal particles are formed during lithiation [42, 43]. Since the experimental voltage is measured from a distribution of nano-sized metal nanoparticles when they were formed, it is impractical to directly compare the average experimental voltage to the calculated voltage at a certain size of metal particle. It is clear, however, that calculation supports the idea that the formation of metal nanoparticles during the conversion reaction could have a lower voltage compared to the thermodynamic voltage of the bulk-phase reaction.

In addition, our computational results indicate that particle size growth leads to increasing  $E^{\text{nano}}$ .  $E^{\text{nano}}$  approaches  $E_{\text{thermodynamic}}^{\text{bulk}}$  when the particle size is larger than 2 nm (Fig. 2(a)) because the nanoscale property of the metal resembles the bulk metal property as the particle size increases. It is reported that when the metal particle gets larger, the integrity of the metal nanoparticle stabilizes because its Gibbs energy per atom decreases (or increment in cohesive energy), and eventually reaches the stability of the bulk metal [27]. This thermodynamic property is associated with Eq. (4) that Gibbs energy of  $\text{M}_n^{\text{cubo or icosa}}$  per atom approaches more negative values when the particle size increases and results in the increment of  $E^{\text{nano}}$ . In our calculations, we did not presume LiF to be a nano-sized phase because LiF is typically a bulk matrix in which metal nanoparticles are distributed.

Importantly, our results also attribute the lower conversion reaction voltage to the surface energy of the metal nanoparticle ( $G_{\text{surface}}^{\text{nano}}$ ). The surface energy as an energy penalty toward the reaction energy needs to be provided to the metal nanoparticle to form during the conversion reaction. We calculated the surface energy of the M nanoparticle ( $M = \text{Fe}, \text{Ni}, \text{Cu}$ ) as a function of its size [44]

$$G_{\text{surface}}^{\text{nano}} = \frac{G^{\text{GGA}}(\text{M}_n^{\text{cubo or icosa}}) - n \cdot G^{\text{GGA}}(\text{M})}{4\pi r^2} \quad (5)$$

where  $G^{\text{GGA}}(\text{M}_n^{\text{cubo or icosa}})$  and  $G^{\text{GGA}}(\text{M})$  are the Gibbs energy of an  $M$  nanoparticle composed of  $n$  atoms and  $M$  bulk metal per atom ( $M = \text{Fe}, \text{Ni}, \text{Cu}$ ), respectively.  $r$  is the average radius which is measured by the distance between the center and vertex atoms of a relaxed nanoparticle (Table S2 in the ESM). It is noted that the surface energy increases as the nanoparticle size decreases (Fig. 2(b)), which results in decrease of the reaction energy and affects the reduction of conversion reaction voltage (Fig. 2(a)). This trend is correlated with the fact that while the particle gets smaller, the fraction of thermodynamically unstable surface atoms increases with respect to the fraction of relatively stable bulk atoms. The cuboctahedron consisting of 309 atoms has 108 atoms (35%) on the surface. As the size decreases, the fraction of surface atoms increases to 92% for the cuboctahedron with 13 atoms. We systematically show the energy penalty in the conversion reaction associated with the formation of metal nanoparticles by first principles, which was conceptually discussed by Cabana et al. [2]. Although the surface energy of nanoparticles is primarily studied in our work, other factors including the crystallinity of the material [45], interfacial energy [46, 47], and electronic conductivity [3] in the nanoscale LiF/M framework can also affect the value and shape of the reaction voltage.

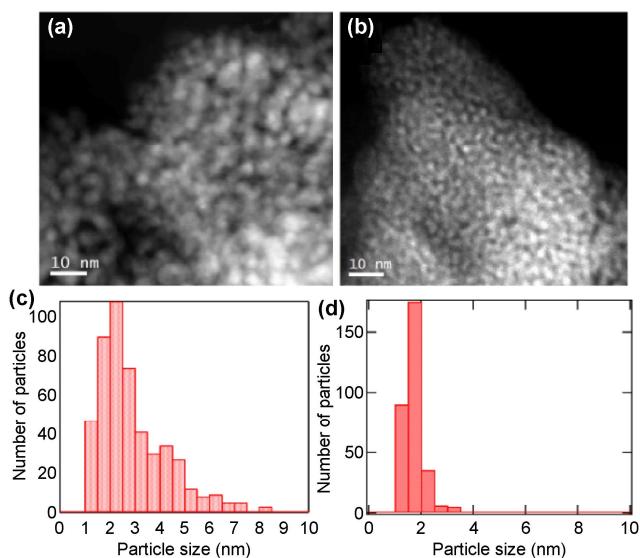
### 3.3 Particle size and electrochemical electrode voltage

The conversion reaction of transition metal difluoride involves local phase nucleation and evolution during the lithiation process. Metal difluoride converts into metal nanoparticle and LiF phases during lithiation. In order to study the correlation of metal nanoparticle formation with conversion reaction voltage in the fully lithiated state,  $\text{CuF}_2/\text{C}$  and  $\text{NiF}_2/\text{C}$  were galvanostatically lithiated (Fig. S1 in the ESM). Various TEM/STEM techniques including SAED patterns, ADF-STEM images, and EELS spectra were used to study the structural and morphological changes of the  $\text{CuF}_2/\text{C}$  and  $\text{NiF}_2/\text{C}$  electrodes during lithiation. We have taken 15 different ADF-STEM images, EELS spectra, and 10 different SAED patterns from various regions of the samples and the representatives of the observed images,

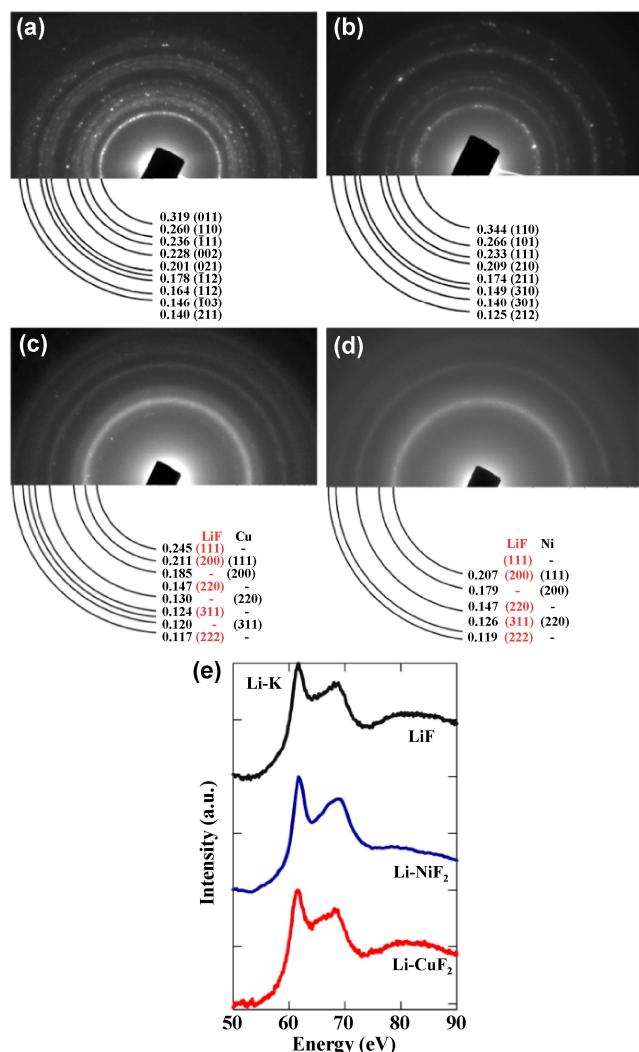
EELS spectra, and SAED patterns are presented here. The bright contrasts in the ADF-STEM image (Fig. 3(a)) correspond to the areas where the highest concentration of Cu can be seen, as ADF-STEM image contrast is highly sensitive to atomic number ( $\sim Z^{1.7}$ ).

The ADF-STEM image of the lithiated NiF<sub>2</sub>/C in Fig. 3(b) shows the distribution of Ni nanoparticles (bright contrast) in a LiF matrix. It is observed that lithiated CuF<sub>2</sub>/C and lithiated NiF<sub>2</sub>/C are composed of Cu and Ni with average particle sizes of ~2.5 and ~1.5 nm, respectively. The particle size distributions of Cu and Ni were obtained from several ADF-STEM images shown in Figs. 3(c) and 3(d). The lithiated CuF<sub>2</sub>/C contained broad particle size ranges from 1 to 10 nm whereas the lithiated NiF<sub>2</sub>/C consisted of Ni particle sizes ranging from 1 to 5 nm. The distinction in average particle sizes is attributed to the differences in diffusion rates of Cu and Ni ions; Cu has a higher diffusivity and thus forms larger particles [14, 16]. The SAED patterns of the pristine CuF<sub>2</sub>/C and NiF<sub>2</sub>/C nanocomposites confirm the existence of a single phase with a monoclinic and tetragonal–rutile structure as shown in Figs. 4(a) and 4(b), respectively.

Upon lithiation, CuF<sub>2</sub>/C with a monoclinic structure converts into a cubic structure consisting of metallic Cu and LiF (Fig. 4(c)). Similarly, NiF<sub>2</sub> with a tetragonal–



**Figure 3** Representative ADF-STEM images of (a) lithiated CuF<sub>2</sub>/C, and (b) lithiated NiF<sub>2</sub>/C. The particle size distribution obtained from several ADF-STEM images of (c) lithiated CuF<sub>2</sub>/C and (d) lithiated NiF<sub>2</sub>/C.



**Figure 4** Representative SAED patterns of (a) pristine CuF<sub>2</sub>/C, (b) pristine NiF<sub>2</sub>/C, (c) lithiated CuF<sub>2</sub>/C, (d) lithiated NiF<sub>2</sub>/C, and (e) Li-K edge EELS spectra of the lithiated CuF<sub>2</sub>/C (Li-CuF<sub>2</sub>), lithiated NiF<sub>2</sub>/C (Li-NiF<sub>2</sub>), and reference LiF.

rutile structure transforms into metallic Ni and LiF upon lithiation, presented in Fig. 4(d). The presence of LiF in lithiated CuF<sub>2</sub>/C and NiF<sub>2</sub>/C is further verified by the characteristic near-edge fine structure in the Li K-edge spectra (Fig. 4(e)).

Interestingly, large Cu particles are found to be isolated and dispersed in the carbon matrix. Figure 5 shows the ADF image and the corresponding energy-dispersive X-ray (EDX) spectra of the lithiated CuF<sub>2</sub>/C.

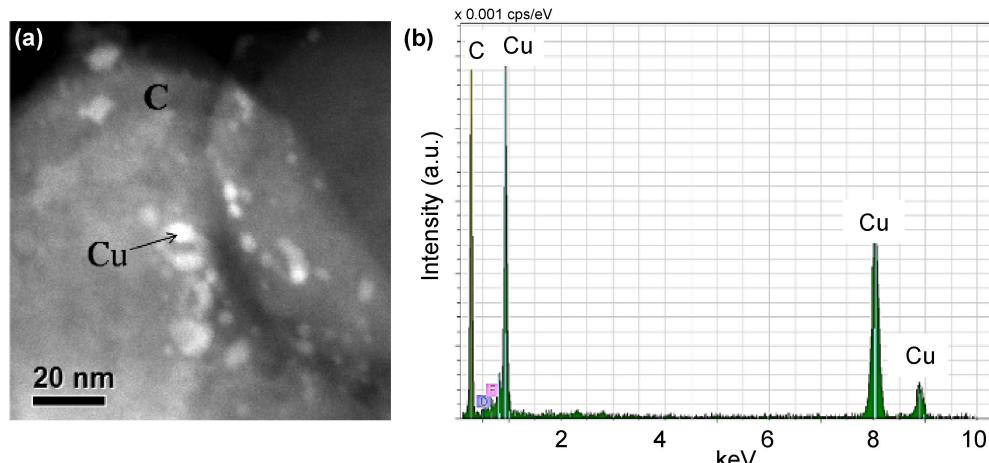
It is observed that large Cu particles (~10 nm) are distributed in the carbon matrix. This suggests that large Cu particles get isolated from LiF after the first discharge; therefore, they most probably have a

reduced chance to participate in the re-conversion reactions.

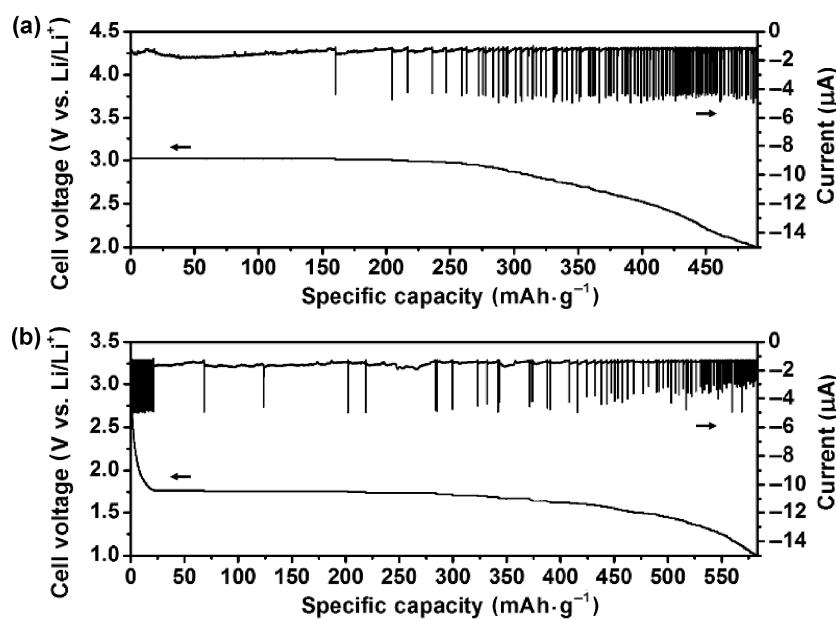
Additionally, PITT was applied to CuF<sub>2</sub>/C and NiF<sub>2</sub>/C cells to measure the conversion reaction voltages at a near-equilibrium state (Fig. 6).

This technique takes small voltage steps and monitors the current correlated with the reaction. We applied a voltage step of 10 mV. The voltage step does not proceed to the next step until the discharge current declines to a current limit of -1.1 and -1.3 μA for CuF<sub>2</sub>/C and NiF<sub>2</sub>/C cells, respectively (C/1,000 for both cells). PITT takes ~ 765 and ~ 909 hours for the first

discharge of CuF<sub>2</sub>/C and NiF<sub>2</sub>/C, respectively. In the case of CuF<sub>2</sub>/C, the open circuit voltage (OCV) was 3.09 V and the conversion reaction proceeded without any significant current decrease to the current limit at 3.02 V (Fig. 6(a)). The reaction continued at the following voltage steps with shortening plateaus. NiF<sub>2</sub>/C had an OCV of 3.07 V and the conversion reaction initiated at 1.77 V after a rapid voltage drop (Fig. 6(b)). From our PITT results, we confirmed that the conversion reactions of both CuF<sub>2</sub>/C and NiF<sub>2</sub>/C occur at lower voltages than the thermodynamic bulk-reaction voltages ( $E_{\text{theoretical}}^{\text{bulk}}$  (CuF<sub>2</sub>) = 3.55 V and



**Figure 5** (a) Representative ADF-STEM and (b) EDX spectrum of the lithiated CuF<sub>2</sub>/C showing the presence of large Cu metal (about 10 nm) on carbon matrix.



**Figure 6** PITT discharges of (a) CuF<sub>2</sub>/C and (b) NiF<sub>2</sub>/C.

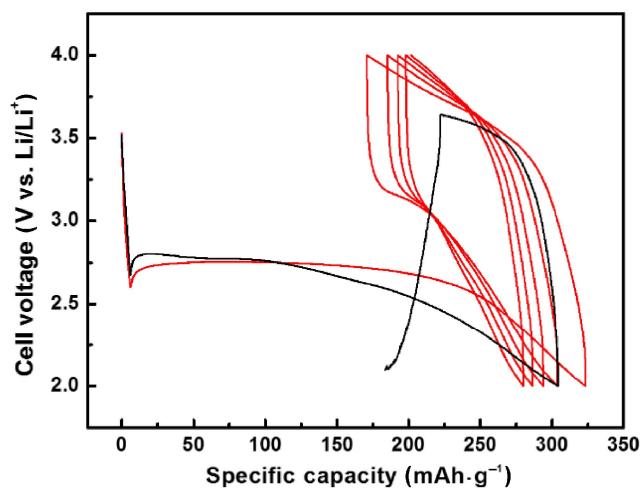
$E_{\text{theoretical}}^{\text{bulk}}$  ( $\text{NiF}_2$ ) = 2.96 V). The formation of metal nanoparticles has a strong influence on the conversion voltage which is lower than the thermodynamic voltage of the bulk-phase reaction.

### 3.4 Rechargeable behavior of $\text{NiO-CuF}_2$ conversion material

According to previous reports, two main factors can result in a poor cycling performance of  $\text{CuF}_2$ : (i) Cu dissolution within the operating voltage window (2.0–4.0 V) [16], and (ii) isolated large Cu particle formation upon lithiation [14]. The linear potential sweep voltammogram for Cu demonstrates that Cu dissolves at ~3.5 V within the operating voltage window of the  $\text{CuF}_2$  electrode (Fig. S2 in the ESM). In addition, our ADF-STEM images exhibited a bimodal Cu particle size distribution (Figs. 3(a) and 5(a)). The small Cu particles (~2.5 nm in average) were distributed in the microstructure of LiF (Fig. 3(a)), which is similar to observations made for other conversion materials including  $\text{FeF}_2$  [48, 49]. However, the large Cu particles (~10 nm) were segregated from LiF and located in the carbon matrix (Fig. 5(a)). It is noteworthy that based on our ADF-STEM image, the majority of Cu particles were observed to be small (~2.5 nm in average) and embedded in LiF (Fig. 3(a)). This contrasts with the previous TEM work on  $\text{CuF}_2$ , which showed that only isolated large Cu particles (5–12 nm) formed upon lithiation [14].

$\text{CuF}_2$  is intrinsically a non-reversible conversion material, in contrast to  $\text{FeF}_2$  and  $\text{NiF}_2$ . However, it has the highest thermodynamic voltage with a theoretical specific capacity of 528  $\text{mAh}\cdot\text{g}^{-1}$ . In the present work, we developed a novel reversible  $\text{NiO-CuF}_2/\text{C}$  electrode. Figure 7 shows the electrochemical voltage profile of  $\text{CuF}_2/\text{C}$  and  $\text{NiO-CuF}_2/\text{C}$  electrodes in the voltage window in the range 2.0–4.0 V at a C/35 rate.

$\text{CuF}_2/\text{C}$  delivered a discharge capacity of 303  $\text{mAh}\cdot\text{g}^{-1}$  (57% of theoretical capacity). Similarly, the  $\text{NiO-CuF}_2/\text{C}$  electrode shows a first discharge capacity of 323  $\text{mAh}\cdot\text{g}^{-1}$  (61% of the theoretical capacity). Both electrodes show quite low voltage plateaus (2.75 and 2.77 V for  $\text{NiO-CuF}_2/\text{C}$  and  $\text{CuF}_2/\text{C}$ , respectively) compared to the thermodynamic voltage of the bulk-phase reaction (3.55 V). However, the  $\text{NiO-CuF}_2/\text{C}$  electrode displays a reversible conversion reaction with specific capacity

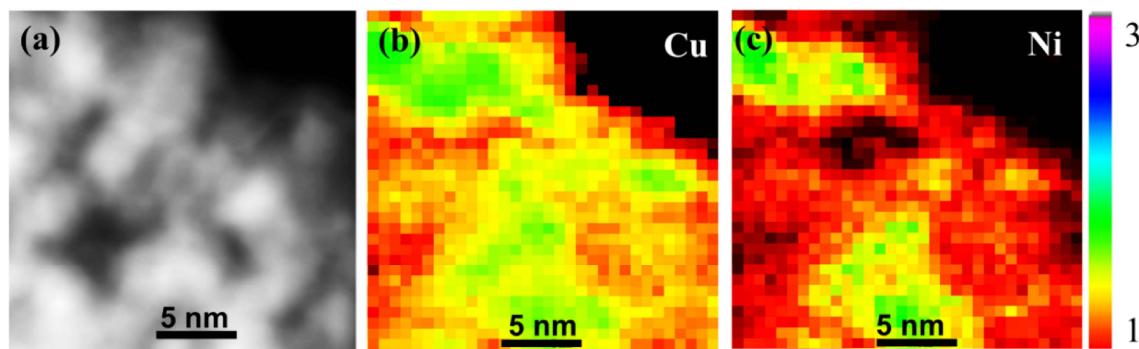


**Figure 7** Voltage profiles of  $\text{CuF}_2/\text{C}$  and  $\text{NiO-CuF}_2/\text{C}$  electrodes.

of 152  $\text{mAh}\cdot\text{g}^{-1}$  during the first charge. During the charging process, the  $\text{CuF}_2/\text{C}$  electrode voltage starts to drop from ~3.64 V resulting in a charge failure. We ascribe this to  $\text{Cu}^{2+}$  dissolution from the cathode.

In order to gain in-depth insights into the effects of NiO on  $\text{CuF}_2$  reversibility, the distribution of Cu and Ni in the lithiated  $\text{NiO-CuF}_2/\text{C}$  sample was studied using STEM-EELS elemental mapping. As lithium and fluoride-based compounds are extremely beam sensitive, we optimized the electron dose and spatial resolution to minimize the beam damage in this work. As such, the STEM-EELS spectrum image is taken with a total electron dose of  $3 \times 10^4 \text{ e}\cdot\text{nm}^{-2}$ . A representative ADF-STEM image and the corresponding  $\text{Cu-L}_{2,3}$  and  $\text{Ni-L}_{2,3}$  edge elemental maps are shown in Fig. 8.

It is observed that the bright contrast is attributed to the areas with the highest concentration of Cu. It is interesting that Ni-rich areas are located in the same regions as Cu-rich areas. It also indicates that the lithiation process mostly occurs in areas with high NiO content. We propose NiO as an artificial solid electrolyte interphase (SEI). NiO is an insoluble solid phase and is electrochemically inactive within the voltage window (2.0–4.0 V), which reduces the direct contact between the cathode and the electrolyte, and possibly alleviates Cu dissolution in the electrolyte. It has been reported that metal oxides could suppress metal ion dissolution into the electrolyte [50–52]. In addition, large Cu particles (~10 nm) are observed in the carbon matrix in the first-time discharged  $\text{NiO-CuF}_2/\text{C}$ . Our ADF-STEM and the corresponding EELS



**Figure 8** Representative ADF-STEM image of (a) the first discharged NiO-CuF<sub>2</sub>/C and the corresponding elemental maps for (b) Cu-L, and (c) Ni-L.

spectra of the first-time discharged NiO-CuF<sub>2</sub>/C (Figs. S3(a), S3(c), and S3(d) in the ESM) showed the presence of large Cu particles (~10 nm) distributed in the carbon matrix, similar to what was found from the lithiated CuF<sub>2</sub>/C (Fig. 5(a)). Interestingly, the large Cu particles were still present in the first-time charged NiO-CuF<sub>2</sub>/C (Figs. S3(b), S3(e), S3(f) in the ESM). This implies that large Cu particles in the carbon domain have less opportunity to participate in further cycles.

To investigate the extent of Cu dissolution into the electrolyte, elemental analysis of the electrolyte was performed using ICP-OES. The first cycled (discharge/charge) CuF<sub>2</sub>/C and NiO-CuF<sub>2</sub>/C cells were disassembled and their electrolytes collected. It is noted that CuF<sub>2</sub>/C cell cannot be charged up to 4 V because of its non-reversible feature in contrast with the NiO-CuF<sub>2</sub>/C cell. For that reason, the electrolyte from the CuF<sub>2</sub>/C cell was collected after the CuF<sub>2</sub>/C cell failed during the charging process. We found that Cu dissolution into the electrolyte was alleviated when the electrode was coated with NiO (Fig. S4 in the ESM). The concentration of Cu in the electrolyte when using CuF<sub>2</sub> electrode was measured to be ~13 ppb; however, the NiO-CuF<sub>2</sub> electrode shows a Cu concentration of ~0 ppb. This observation directly indicates that NiO coating suppresses Cu dissolution and alleviates electrode degradation.

Recently, a bimodal-size evolution of Ni nanoparticles from NiO-NiF<sub>2</sub>/C electrode has been reported by pair distribution function (PDF) analysis, and that NiO possibly facilitates the conversion process by providing electronic conductivity [3]. The NiF<sub>2</sub>/C electrode, however, is only converted into smaller Ni nano-

particles because of its insulating property. In order to investigate the phase transformation in CuF<sub>2</sub>/C and NiO-CuF<sub>2</sub>/C, we also conducted PDF for (a) first-time discharged CuF<sub>2</sub>/C, (b) first-time discharged NiO-CuF<sub>2</sub>/C, (c) first-time charged NiO-CuF<sub>2</sub>/C, and (d) second-time discharged NiO-CuF<sub>2</sub>/C samples, as shown in Fig. S5 in the ESM. We measured the Cu phase with average nanoparticle size of ~2.3 nm from the second-time discharged NiO-CuF<sub>2</sub>/C (Fig. S5(d) in the ESM). Cu<sub>2</sub>O are mainly found from the other samples instead of the Cu phase (Figs. S5(a)–S5(c) in the ESM), which is most likely to have resulted from the contamination of samples by air when they were kept in Kapton capillaries [16]. Although more PDF work is needed, our PDF refinement on the second-time discharged NiO-CuF<sub>2</sub>/C confirms the formation of Cu nanoparticles, which suggests that NiO facilitates the CuF<sub>2</sub>/C reversible reaction.

#### 4 Conclusions

In this study, we combined first principles calculations and experiments with characterization techniques to analyze the conversion reaction voltage for MF<sub>2</sub>(M = Fe, Ni, Cu) in Li-ion batteries. Based on our calculations, the voltage heavily depends on the size of metal nanoparticle generated. The formation of metal nanoparticles affects the conversion reaction voltage, which is lower than the thermodynamic voltage of the bulk-phase reaction. We propose that the surface energy of metal nanoparticle is an energy penalty against the free energy of reaction, bringing about a reduced voltage. Our ADF-STEM images demonstrated Cu and Ni



nanoparticle formations for the first discharged CuF<sub>2</sub> and NiF<sub>2</sub>, respectively. Similarly, the PITT results show that the conversion reactions of CuF<sub>2</sub> and NiF<sub>2</sub> occur at lower voltages as a result of metal nanoparticle formation.

Moreover, we developed a rechargeable CuF<sub>2</sub> electrode by introducing NiO. We propose that NiO reduces the immediate contact between the CuF<sub>2</sub> and the electrolyte, thus suppressing Cu dissolution. We suggest that NiO can be used as an artificial SEI layer to improve the reversibility of Cu-based conversion materials. Further research on surface coatings will provide a breakthrough in the class of high energy density conversion materials.

## Acknowledgements

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**Electronic Supplementary Material:** Supplementary material (further details of average radius of nanoparticle, bulk-phase reaction voltages, comparison of lattice parameters, the first discharge curves, linear potential sweep voltammogram, ADF-STEM images and EELS spectra, ICP-OES data, and experimental PDF profiles) is available in the online version of this article at <http://dx.doi.org/10.1007/s12274-016-1365-6>.

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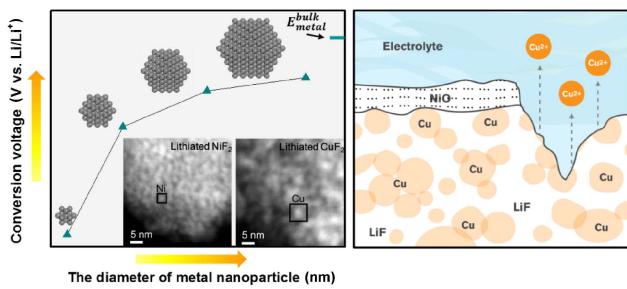
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## Table of contents



The conversion reaction voltage in the Li ion battery is reinterpreted based on the size of metal nanoparticles. A reversible CuF<sub>2</sub> electrode is developed by coating with NiO.



## Electronic Supplementary Material

# Revisiting the conversion reaction voltage and the reversibility of the CuF<sub>2</sub> electrode in Li-ion batteries

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**Table S1** Comparison of lattice parameters between GGA + *U* calculation and experiments

	Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)
GGA + <i>U</i> calculation	CuF <sub>2</sub>	3.32 (1.06%)	4.617 (1.20%)	4.671 (1.19%)	82.756 (0.65%)
	NF <sub>2</sub>	4.696 (1.00%)	4.696 (1.00%)	3.104 (0.67%)	90.0000
	FeF <sub>2</sub>	4.788 (1.99%)	4.788 (1.99%)	3.3.16 (0.18%)	90.0000
Experimental	CuF <sub>2</sub>	3.297	4.562	4.616	83.293
	NF <sub>2</sub>	4.650	4.650	3.084	90.0000
	FeF <sub>2</sub>	4.695	4.695	3.310	90.0000

We adopt *U* as 4.0, 6.0, and 4.0 for Fe, Ni, and Cu, respectively [S1]. The percentage in parenthesis shown in Table S1 represents the deviation ratio of lattice parameters calculated from GGA + *U* calculation, with respect to experimental data [S2, S3].

**Table S2** The average radius of M (M = Fe, Ni, and Cu) nanoparticle composed of *n* atoms

<i>n</i>	Iron		Nickel		Copper	
	Cubotahedron	Icosahedron	Cuboctahedron	Icosahedron	Cuboctahedron	Icosahedron
13	2.44 Å	2.40 Å	2.37 Å	2.32 Å	2.47 Å	2.41 Å
55	4.85 Å	4.75 Å	4.80 Å	4.60 Å	4.94 Å	4.81 Å
147	7.25 Å	7.04 Å	7.26 Å	7.01 Å	7.49 Å	7.29 Å
309	9.94 Å	9.30 Å	9.71 Å	9.39 Å	10.03 Å	9.74 Å

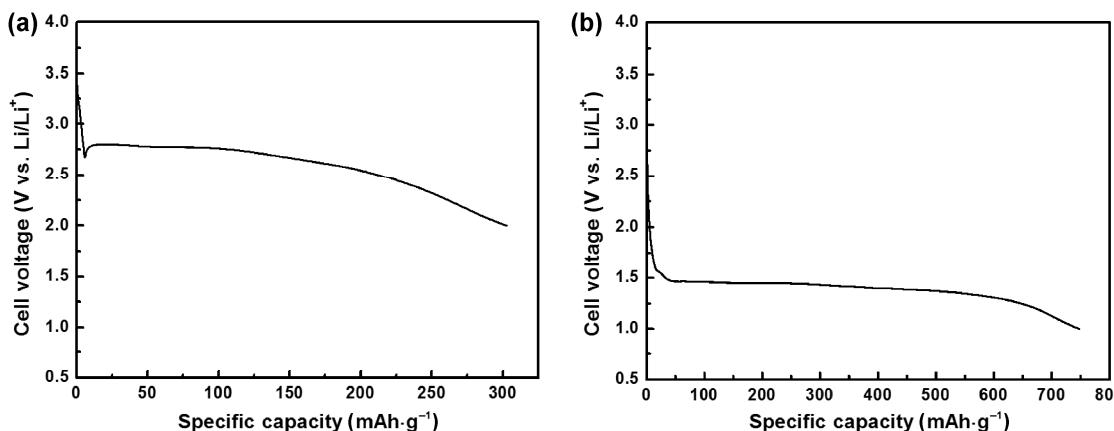
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All nanoparticle morphologies are fully relaxed. The average distance between the center and vertex atoms is defined as a radius of M (M = Fe, Ni, and Cu) nanoparticle composed of  $n$  atoms shown in Table S2.

**Table S3** Bulk-phase reaction voltages calculated from GGA, mixing GGA/GGA +  $U$ , and Gibbs free energy of formation in thermodynamic table

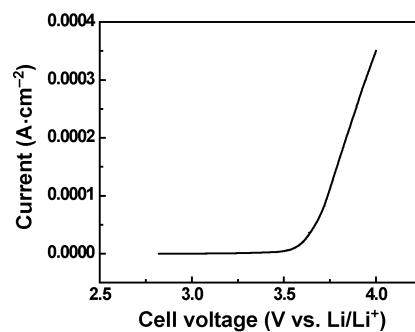
Method	FeF <sub>2</sub>	NiF <sub>2</sub>	CuF <sub>2</sub>
GGA	3.06 V	3.46 V	3.70 V
Mixing GGA/GGA + $U$ (this work)	2.58 V	2.91 V	3.56 V
Gibbs free energy and formation (thermodynamic table)	2.66 V	2.96 V	3.55 V

The voltage calculated from mixing GGA/GGA +  $U$  shows less than 0.09 V difference compared to the voltage measured from thermodynamic table as shown in Table S3. GGA calculations, however, overestimate voltages up to  $\sim 0.50$  V. Therefore we apply mixed GGA/GGA +  $U$  scheme throughout the study.



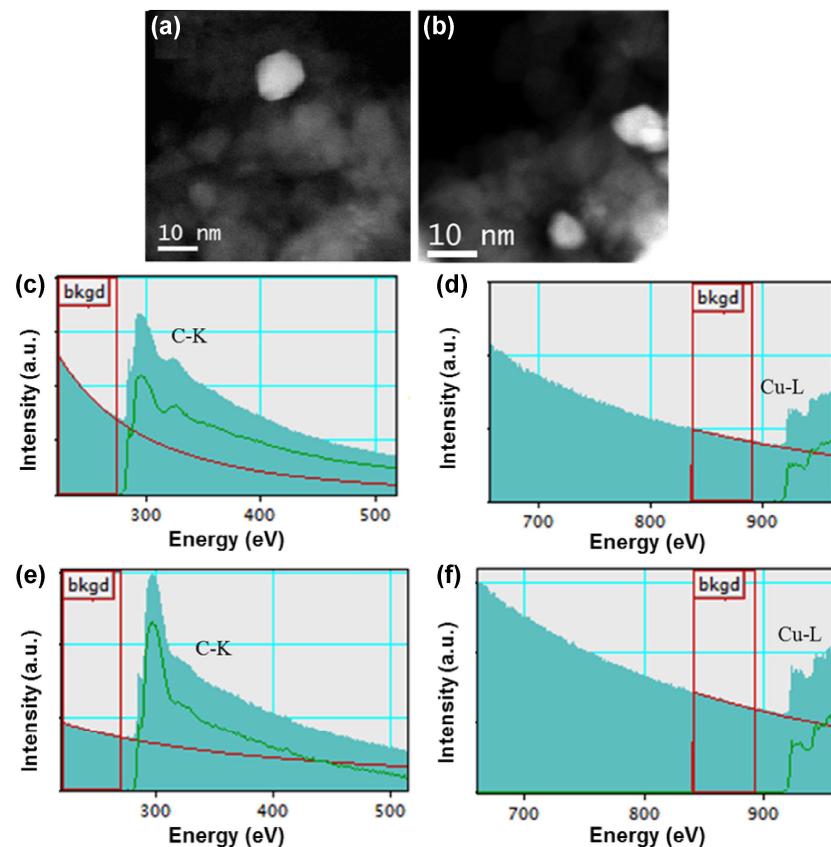
**Figure S1** The first discharge of (a) CuF<sub>2</sub>/C and (b) NiF<sub>2</sub>/C.

The first discharge of CuF<sub>2</sub>/C and NiF<sub>2</sub>/C are tested with the constant current density of C/35. The voltage limit is 2.0 and 1.0 V for CuF<sub>2</sub>/C and NiF<sub>2</sub>/C, respectively.



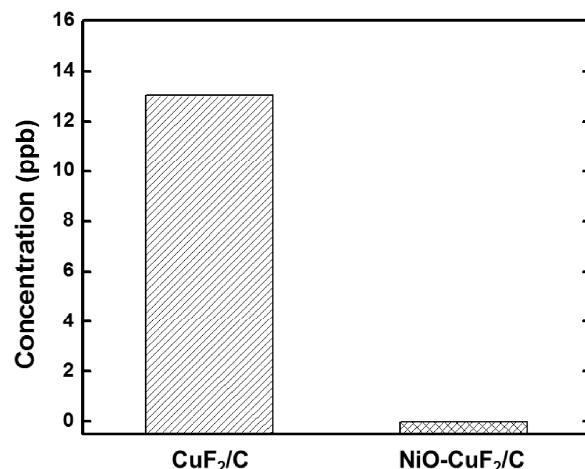
**Figure S2** Linear potential sweep voltammogram for Cu foil.

Linear potential sweep voltammogram for Cu foil is conducted as shown in Fig. S2. Cu foil is employed for the working electrode. We use a pure lithium metal as a counter electrode and a polypropylene C480 (Celgard) as a separator. The coin cell (2016) is assembled with the electrolyte consisting of 1 M LiPF<sub>6</sub> dissolved in EC and DMC with a weight ratio of 1:1 (BASF) in the MBraun Ar-filled glovebox (H<sub>2</sub>O < 0.1 ppm). A Solartron 1,287 electrochemical interface is used to perform the linear potential sweep voltammogram with the scan rate of 1 mV·s<sup>-1</sup>.



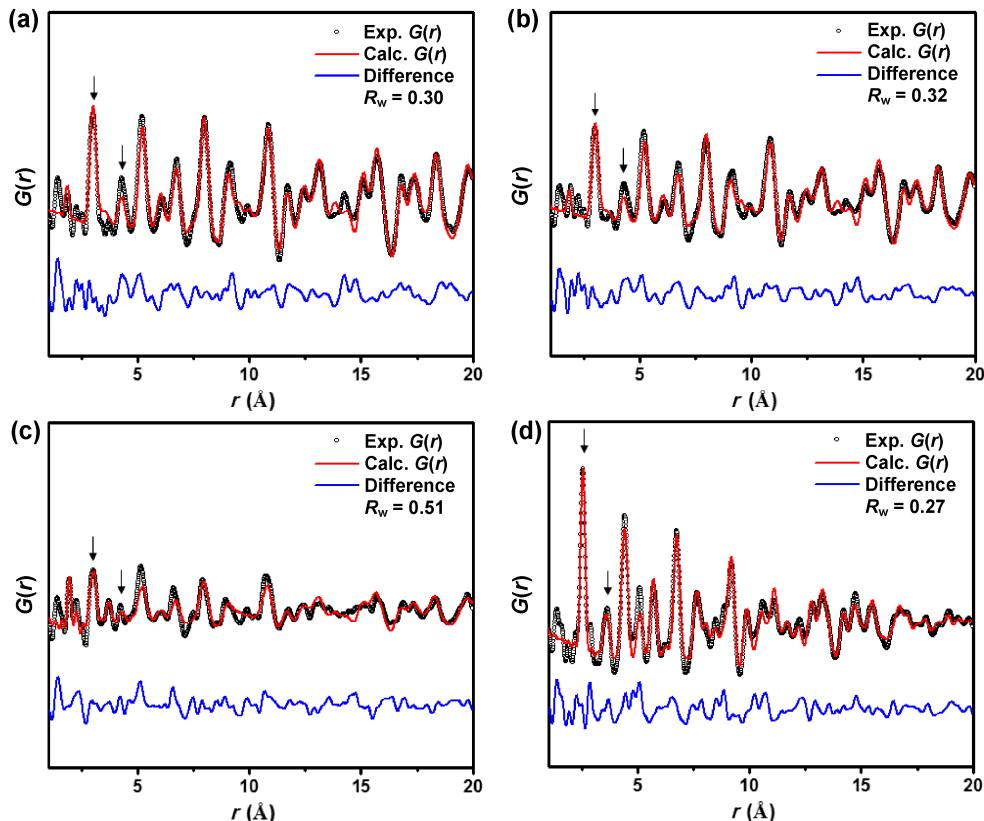
**Figure S3** ADF-STEM of (a) the first discharged and (b) the first charged NiO-CuF<sub>2</sub>/C. C-K edge EELS spectra of (c) the first discharged and (e) the first charged NiO-CuF<sub>2</sub>/C. Cu-L edge EELS spectra of (d) the first discharged and (f) the first charged NiO-CuF<sub>2</sub>/C.

Figure S3(a) exhibits the ADF-STEM image of the first discharged NiO-CuF<sub>2</sub>, showing large copper particles with bright contrast in carbon matrix. The corresponding EELS spectra are displayed in Figs. S3(c) and S3(d), which confirms the presence of metallic copper and carbon, and nonexistence of F-K edge (around 690 eV) from LiF phase. The presence of large copper particles in carbon matrix can still be observed after the first charge (Figs. S3(b), S3(e), and S3(f)). This further validates that the large copper particles are isolated from LiF phase and do not participate in the first charge.



**Figure S4** Cu dissolution into the electrolyte from CuF<sub>2</sub>/C and NiO-CuF<sub>2</sub>/C electrodes.

Cu dissolution is measured by ICP-OES as shown in Fig. S4. A custom-made cell consisting of a CuF<sub>2</sub>/C (or NiO-CuF<sub>2</sub>/C), a pure lithium metal, a polypropylene C480 (Celgard) is assembled with 1 M LiPF<sub>6</sub> dissolved in EC and DMC with a weight ratio of 1:1 (BASF) in the MBraun Ar-filled glovebox (H<sub>2</sub>O < 0.1 ppm). The first cycled (discharge/charge) CuF<sub>2</sub>/C and NiO-CuF<sub>2</sub>/C cells are disassembled and the electrolyte is collected to perform ICP-OES.



**Figure S5** Experimental PDF (Exp.  $G(r)$ ), refined fit (Calc.  $G(r)$ ), and difference between Exp.  $G(r)$  and Calc.  $G(r)$ . (a) The first discharged CuF<sub>2</sub>/C, (b) first discharged NiO-CuF<sub>2</sub>/C, (c) first charged NiO-CuF<sub>2</sub>/C, and (d) second discharged NiO-CuF<sub>2</sub>/C.

We collect high-energy total X-ray scattering data ( $\lambda = 0.2114 \text{ \AA}$ ) at the PDF beamline 11-ID-B of the Advanced Photon Source in Argonne National Laboratory as shown in Fig. S5. We integrate raw images by using the software FIT2d [S4]. PDFgetX2 [S5] is utilized to correct the data for background contributions, Compton scattering, and detector effects. Fourier transform is conducted to generate  $G(r)$ , the PDF. We refine PDF data using PDFgui [S6]. The electrode samples are (a) first discharged CuF<sub>2</sub>/C, (b) first discharged NiO-CuF<sub>2</sub>/C, (c) first charged NiO-CuF<sub>2</sub>/C, and (d) second discharged NiO-CuF<sub>2</sub>/C. CuF<sub>2</sub>/C sample is discharged to 2 V, and NiO-CuF<sub>2</sub>/C samples are discharged and charged to 2.0 and 4.0 V, respectively. Samples are obtained by disassembling the coin cells inside the Ar-filled glovebox. We wash electrodes with battery-grade DMC (Novolyte) and seal them in Kapton under Ar atmosphere.

The PDF analysis of X-ray total scattering data is applied to understand phase transformations during conversion reactions. The structural refinement on the first discharged CuF<sub>2</sub>/C demonstrates the formation of Cu<sub>2</sub>O. The peaks at 3.0 Å and 4.3 Å correspond to the first and second nearest Cu–Cu bonds in Cu<sub>2</sub>O, respectively (Fig. S5 (a)). This phase has a cubic structure with the space group of  $Pn\bar{3}m$ . The PDF analysis for the first discharged and the first charged NiO-CuF<sub>2</sub>/C also exhibits peaks at 3.0 Å and 4.3 Å representing Cu–Cu bonds in Cu<sub>2</sub>O (FigS. S5(b) and S5(c)). The second discharged NiO-CuF<sub>2</sub>/C indicates peaks at 2.6 and 3.6 Å

which are corresponding to the first and second nearest Cu–Cu bonds in Cu, respectively (Fig. S5(d)). Cu is a cubic structure with the space group of  $Fm\bar{3}m$ . The structural refinement on PDF for the second discharged NiO-CuF<sub>2</sub>/C implies the formation of Cu nanoparticle with ~2.3 nm in diameter.

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