Fluoride ion batteries (FIBs) are a recent alternative all-solid-state battery technology. However, the FIB systems proposed so far suffer from poor cycling performance. In this work, we report La$_2$NiO$_{4+\delta}$ with a Ruddlesden-Popper type structure as an intercalation-based active cathode material in all solid-state FIB with excellent cycling performance. The critical charging conditions to maintain the conductivity of the cell were determined, which seems to be a major obstacle towards improving the cycling stability of FIBs. For optimized operating conditions, a cycle life of about 60 cycles and over 220 cycles for critical cut-off capacities of 50 mAh/g and 30 mAh/g, respectively, could be achieved, with average Coulombic efficiencies between 95 – 99%. Cycling of the cell is a result of fluorination/de-fluorination into and from the La$_2$NiO$_{4+\delta}$ cathode, and it is revealed that La$_2$NiO$_{4+\delta}$ is a multivalent electrode material. Our findings suggest that La$_2$NiO$_{4+\delta}$ is a promising high energy cathode for FIBs.
The current market of portable energy storage systems is dominantly covered by lithium ion batteries (LIBs) due to their unique electrochemical performance including a high potential window, high energy density, reasonable capacity, and excellent cycle life. While there is little concern about the shortage of reserves of elements in use on a short term, there is a controversy debate about the availability of sufficient reserves of critical elements (such as Li, Co) in long-term future, especially with the increase of electromobility and non-mobile energy storage technologies. Further, owing to safety concerns there are needs for all solid-state batteries when it comes to future battery technologies. Li-ion batteries based on different shuttling ions and electrode materials, aiming to obtain similar performances as LIBs.

One of the alternatives that has been considered recently are so-called fluoride ion batteries (FIBs), which are based on the shuttling of fluoride ions. Since fluoride is the most stable anion with a high mobility, FIBs can theoretically provide a very wide potential window. Apart from some limited reports on primary batteries based on fluoride ions in the 1970s, the first report on electrochemical rechargeable FIBs was proposed at 2011 by Fichtner et al., based on an all-solid-state battery with La$_{0.5}$B$_{0.2}$F$_{1.9}$ as the solid electrolyte and conversion-based metal fluorides as active electrodes (e.g., CuF$_2$, BiF$_3$, and SnF$_2$ as the active cathode materials). Since then, the efforts on investigating such systems were further increased, addressing the development of solid electrolytes and improved cell designs as well as the screening of conversion-based electrodes.

The principle advantage of conversion-based materials would lie in their high specific capacity (e.g., ~190 mAh/g for Bi/CF$_3$$_7$7, 270 mAh/g for Bi/Mg-MF$_2$$_7$3, and ~400 mAh/g for Cu/Mg-MF$_2$$_7$3 electrochemical cells); however, such systems suffer from a strong capacity fading for higher cycle numbers (for example, the capacity reduces to ~10% of its initial value after the first cycle). Electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) reveal that, although the carbon additive is affected within a side reaction on charging, stable cycling can be obtained by reducing the cutoff capacities with respect to the maximum capacity. In addition, the phase behavior of La$_2$NiO$_{4+d}$ was found to be complex. Therefore, the La$_2$NiO$_{4+d}$F$_n$ fluorinated phase has been further investigated by means of transmission electron microscopy (TEM) techniques (imaging, automated diffraction tomography (ADT) and energy-dispersive X-ray (EDX) spectroscopy) together with X-ray absorption spectroscopy (XAS), confirming nearly full occupation of the interstitial sites by anions and successful formation of a high fluorine content phase of La$_2$NiO$_{4.13}$F$_{1.59}$.

Results and Discussion

Electrochemical charging and the fluorination behavior of La$_2$NiO$_{4+d}$

The compound La$_2$NiO$_{4+d}$ formed after solid-state synthesis has an approximate composition of La$_2$NiO$_{4.13}$ (d = 0.13). From this, a theoretical maximum capacity of 125 mAh/g for the formation of La$_2$NiO$_{4.13}$F$_{1.87}$ can be expected if one assumes a simple filling of all empty interstitial anion sites, according to the following reaction equation:

$$\text{La}_2\text{NiO}_{4.13} + 1.87 \text{F}^- \rightarrow \text{La}_2\text{NiO}_{4.13}\text{F}_{1.87} + 1.87 \text{e}^-.$$ 

Schematic illustrations of the un-fluorinated La$_2$NiO$_{4.13}$ and fluorinated La$_2$NiO$_{4.13}\text{F}_{1.87}$ state have been plotted in Fig. 1.

As described in “Methods,” the active La$_2$NiO$_{4+d}$ cathode material has been mixed (and ball milled) with the La$_{0.9}$Ba$_{0.2}$F$_{1.9}$ electrolyte material and carbon nanotubes (CNTs) in order to improve the ionic and electronic conductivity of the cell, respectively. Supplementary Fig. 1 shows scanning TEM (STEM)
images of the synthesized cathode composite material before charge, which gives an indication that the electrolyte and CNTs agglomerate at the surface of the active cathode material. This is desirable from the ionic and electronic conductivity point of view. However, even partial coverage of the active cathode material by the solid electrolyte and the carbon additive prohibits a detailed analysis of the changes of the La$_2$NiO$_{4.13}$ particles on charging by means of surface-sensitive techniques such as XPS, since the spectra become strongly dominated by the carbon and electrolyte species (see "Discussion" within Supplementary Notes). In this respect, other techniques including Fast-ADT, EDX, and XAS were used in order to understand the structural changes of the La$_2$NiO$_{4.13}$ cathode material on charging the cell, which will be discussed later in this section.

In order to investigate the structural changes that are expected to occur on F$^-$ anion incorporation into Ruddlesden–Popper-type compounds during the electrochemical charging step, different La$_2$NiO$_{4+d}$/Zn-ZnF$_2$ cells were galvanostatically charged to various cutoff capacities up to 155 mAh/g. Figure 2a represents the charging curves showing excellent reproducibility regardless of the use of different cells. The charging curve can be divided into three regions. The starting potential of the La$_2$NiO$_{4+d}$/Zn-ZnF$_2$ cell is at about 0.8 V (start of the region (I)) followed by a sharp increase in the voltage up to ~1.7 V over a small capacity range of 10 mAh/g. Since the initiation of the electrochemical reaction often involves several steps including overcoming the chemical activation energy barrier, mass transfer, and adsorption of electroactive material, such an increase in overvoltage is reasonable. At 1.7 V, a fairly flat plateau with an increase to ~2.0 V over a capacity range of ~130 mAh/g can be observed (region (II)). In this region, strong structural changes are observed within the cathode composite with respect to the Ruddlesden–Popper phase. The respective XRD measurements...
and corresponding lattice parameters after charging the La$_2$NiO$_{4+d}$/Zn-ZnF$_2$ cell to various cutoff capacities up to 155 mAh/g are plotted and listed in Fig. 2b–d and Table 1, respectively. The XRD pattern of the initial La$_2$NiO$_{4+d}$ active cathode material before charging can be fitted in the tetragonal crystal system, space group I4/mmm (a$^2 = b^2 =$ 5.463(4) Å and c = 12.671(10) Å), which is the highest symmetry of the n = 1 Ruddlesden–Popper-type structure. After electrochemical charging of the cell up to 10 mAh/g, two phases can be observed (Fig. 2c): the first phase is similar to the original La$_2$NiO$_{4+d}$ with tetragonal unit cell and the second phase is an orthorhombic phase with increased lattice parameter a and decreased lattice parameter b (as shown in Fig. 2c), resulting from the small change in composition compared to the original La$_2$NiO$_{4+d}$. Owing to the fact that no superstructure reflections could be observed, all orthorhaphic phases were refined using the highest symmetry orthorhombic space group of Fmmm, which can be derived from the aristotype I4/mmm symmetry for a $\sqrt{2} \times \sqrt{2} \times 1$ supercell. Such an orthorhombic distortion was also found previously in La$_2$NiO$_4$F$_2$, which was prepared via a non-oxidative fluorination of La$_2$NiO$_{4+d}$ using polyvinylidene fluoride and resulted from ordering of vacancies, unresolved within the composite mixtures used here. The orthorhombic distortion of this phase increases on further charging to 30 mAh/g (see Fig. 2c and Table 1), and the phase disappears at capacities >30 mAh/g. Then, a third La$_2$NiO$_{4+d}$F$_{2+y}$ (fluorine rich with orthorhombic space group Fmmm) phase can be found, where the large expansion of the c-axis (c ~ 15.2 Å compared to c ~ 12.7 Å for La$_2$NiO$_{4+d}$) is indicative for the strong fluorination of the material (see Fig. 2b, Supplementary Fig. 2a, and Table 1). The relative weight fraction of the La$_2$NiO$_{4+d}$F$_{2+y}$ phase increases with increasing charging capacity and reaches to approximately 77 wt-% at 155 mAh/g as is shown in Fig. 2d. Importantly, especially at the higher capacities within regions (II)/(III), a strong decrease of the overall amount of the La$_2$NiO$_4$ phase. It is also worth emphasizing that the XRD measurements do not indicate any significant decomposition of the La$_2$NiO$_{4+d}$F$_{2+y}$ electrolyte material (see Supplementary Table 1), which is plausible with respect to its wide electrochemical stability window reported previously (ca. –1.8 to +3.7 V against Zn/ZnF$_2$).

Note that no significant structural changes can be detected in the anode material after charging (and discharging) since the Zn-ZnF$_2$ anode material has been used in a high excess (see Supplementary Fig. 2b). This is in accordance with the previous studies on the M-MF$_2$ (M = Pb, Zn) anode materials for intercalation-based La$_2$CoO$_4$ cathode material for FIBs. XPS measurement also does not show a significant change in the spectra of the anode material between the uncharged and charged (to 120 mAh/g) samples, as expected (please see Supplementary Fig. 3).

In addition, a partial oxidation of the carbon matrix is overlying the charging of La$_2$NiO$_{4+d}$/Zn-ZnF$_2$ cell to various cutoff capacities at ~1.70 V and current density of 24 A/cm$^2$. Prior to deintercalation, the XPS and Raman measurements, which will be fully discussed later with respect to the different changes happening within the CNT in the different regions. Therefore, a cutoff capacity of around 135 mAh/g must be considered to be the highest charging capacity before an extended destruction of the conductive carbon matrix takes place, which would result in an immediate deterioration of the discharge behavior.

Since the electrochemical fluorination of La$_2$NiO$_{4+d}$ overlaps with these side reaction(s), determination of the fluorine content from the length of the charging plateau is not possible (e.g., as can be done for La$_2$CoO$_4$, with its separated plateau). This is also evident from the low Coulombic efficiency within the first cycle,

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**Table 1** State of charge-dependent lattice parameters of the RP-type phase.

| Cutoff capacity (mAh/g) | La$_2$NiO$_{4+d}$ (phase 1)/Fmmm | La$_2$NiO$_{4+d}$F$_{2+y}$/Fmmm |
|-------------------------|----------------------------------|---------------------------------|
|                         | a (Å)   | b (Å)   | c (Å)   | V (Å³)     | a (Å)   | b (Å)   | c (Å)   | V (Å³)     |
| Before charge           | 5.460 (1) | 5.465 (1) | 12.671 (2) | 378.1 (1) | 5.400 (1) | 5.400 (1) | 12.686 (4) | 394.4 (1) |
| 10                      | 5.455 (1) | 5.460 (1) | 12.686 (2) | 378.6 (1) | 5.400 (1) | 5.400 (1) | 12.691 (4) | 394.4 (1) |
| 50                      | 5.443 (1) | 5.458 (1) | 12.691 (2) | 378.7 (1) | 5.390 (1) | 5.390 (1) | 12.696 (4) | 394.5 (1) |
| 90                      | 5.447 (1) | 5.458 (1) | 12.706 (2) | 379.1 (1) | 5.390 (1) | 5.390 (1) | 12.711 (4) | 394.6 (1) |
| 110                     | 5.438 (1) | 5.458 (1) | 12.711 (2) | 378.6 (1) | 5.380 (1) | 5.380 (1) | 12.716 (4) | 394.7 (1) |
| 155                     | 5.449 (1) | 5.458 (1) | 12.736 (3) | 380.1 (2) | 5.390 (2) | 5.390 (2) | 12.741 (6) | 395.4 (3) |

RD structural data of the La$_2$NiO$_{4+d}$/Zn-ZnF$_2$ cathode material shows the presence of different crystal phases at ~1.70 V and current density of 24 A/cm$^2$. 
as is shown previously. Redox titrations of phase pure chemically fluorinated samples would be the method of choice for determining the fluorine content of the samples and average Ni oxidation state. Attempts were made to prepare phase pure fluorinated phase (La2NiO4+dFy) by means of a variety of oxidative fluorination methods (mild fluorination reactions using CuF2 in oxygen (see Supplementary Fig. 4a) as well as F2 gas at various concentrations, reaction times, and temperatures (see Supplementary Fig. 4b, c)). Regardless of the approach used, we could not form high amounts of the fluorinated phase with lattice parameter c of ~15.2 Å (for more information, please see Supplementary Notes). Further, XPS methods did not serve to analyze the oxidation state of Ni content and Ni oxidation state, which combines electron diffraction analysis, EDX, and XANES analysis. The quality of the Fast-ADT data was good enough for crystal determination within the space group $I4_1/mcm$ (0.030 ≤ d ≤ 0.17) as compared to the La2NiO4+dFy (after electrochemical fluorination up to 120 mAh/g with a current density of +24 μA/cm² at 170 °C) in agreement with the results of electron diffraction analysis, EDX, and DFT calculations; changes in the Ni oxidation state with respect to the absorption edge energies.

The reconstruction of the observed diffraction space allowed the identification of the unit cell in the orthorhombic setting for both crystals: $a = 5.50$ Å, $b = 5.47$ Å, $c = 12.63$ Å for the un-fluorinated phase (La2NiO4+d), and $a = 5.37$ Å, $b = 5.31$ Å, $c = 14.45$ Å for the fluorinated phase (La2NiO4+dFy). Supplementary Fig. 5 shows the projections of the reconstruction of the observed diffraction space along the main axes of the fluorinated phase that allowed the determination of the cell. These results well confirm the expansion of the cell along the c axis (contraction of the $a$ and $b$ axes) on fluorine insertion at the interstitial sites of the La2NiO4+d host. This is in a good agreement with the changes in the lattice parameters obtained by the XRD measurements (see Table 1), if we take into account that lattice parameters from electron diffraction are less accurate because of the camera length variation due to the electromagnetic lenses.

The quality of the Fast-ADT data was good enough for crystal structure determination through direct methods and further refinement within the space group $Fmmmm$. Structure refinement using the dynamical scattering theory was possible for the un-fluorinated phase but the reflection quality of the fluorinated phase only allowed to perform a kinematical refinement. Nevertheless, both crystal refinements converged with good and acceptable R1 values for electron diffraction (see Supplementary Table 2 for further details; structural parameters extracted from the refinement can be found in Supplementary Table 3). The degree of fluorination can be approximated from the refined interlayer occupancy indicating a composition of La2NiO4X1.72.
Table 2 Bond distances of Ni-O.

|                  | La\textsubscript{2}NiO\textsubscript{4} calculated | Un-fluorinated particle from Fast-ADT | La\textsubscript{2}NiO\textsubscript{4}F calculated | La\textsubscript{2}NiO\textsubscript{4}F\textsubscript{2} calculated | Fluorinated particle from Fast-ADT |
|------------------|--------------------------------------------------|--------------------------------------|---------------------------------------------------|---------------------------------------------------|-----------------------------------|
| \(d_{equatorial}\) (Å) | 1.94                                             | 1.93                                 | 2.01                                              | 1.97                                              | 1.89                              |
| \(d_{apical}\) (Å)   | 2.24                                             | 2.17                                 | 2.05                                              | 1.88                                              | 1.90                              |
| \(d_{average}\) (Å)  | 2.09                                             | 2.05                                 | 2.03                                              | 1.93                                              | 1.90                              |

The values given are based on the structural models determined via Fast-ADT and from DFT-based calculations.

Fig. 4 CV measurements on La\textsubscript{2}NiO\textsubscript{4+x}. a Cyclic voltammograms of La\textsubscript{2}NiO\textsubscript{4+1.3} vs. Zn–ZnF\textsubscript{2}. b Cyclic voltammograms of La\textsubscript{2}NiO\textsubscript{4+1.3} vs. Pb–PbF\textsubscript{2}. Both measurements were performed by a scan rate = 0.1 mV/s at \(T = 170^\circ\text{C}\).

for the fluorinated phase, which corresponds to a Ni oxidation state of \(\sim +3.85\) for \(d = 0.13\) (La\textsubscript{2}Ni\textsubscript{2}O\textsubscript{4+1.5}F\textsubscript{1.59}) and \(+3.72\) for \(d = 0\) (La\textsubscript{2}Ni\textsubscript{2}O\textsubscript{4+1.72}). In contrast, the interstitial site was found to be unoccupied for the un-fluorinated particle. This agrees well with the complementary elemental analyses via EDX, from which compositions of La\textsubscript{2}Ni\textsubscript{2}O\textsubscript{4+1.5}F\textsubscript{1.8} (nearly fully filled interstitial sites) and La\textsubscript{2}NiO\textsubscript{4} (nearly empty interstitial sites) can be approximated for fluorinated and un-fluorinated crystals, respectively (please see Supplementary Fig. 6 and Supplementary Table 4). XAS indicates a clear shift in the absorption spectrum to higher energies for the charged sample in comparison to uncharged (La\textsubscript{2}Ni\textsubscript{2}O\textsubscript{4+1.3}), as can be seen in Fig. 3c, d (detailed X-ray absorption edges can be found in Supplementary Table 5).

Furthermore, reference samples of known compositions and oxidation states are also plotted for comparison (please see Supplementary Table 6 for the composition of the reference phases). This energy shift (\(\sim 1.3\) eV, see Fig. 3c, d) matches well with what would be expected from the average oxidation state after charging (which can be determined from the refined phase fractions and the average oxidation states estimated from the crystallographic analysis of Fast-ADT). The absence of changes between the spectra in the prepeak area as well as in the white line confirms a similar coordination geometry of Ni and therefore a pure electronic effect (change in oxidation state), which causes the energy shift of the spectra.

DFT structure optimizations were performed for the different compositions La\textsubscript{2}Ni\textsubscript{2}O\textsubscript{4+x} (\(0 \leq x \leq 2\), \(\Delta = 0.5\)) and show that the \(c\)-axis tends to increase more strongly for fluorination degrees \(x > 1\), reaching a value of \(\sim 15.2\) Å for \(x = 2\) (see Supplementary Fig. 7a). In addition, the contraction within the \(ab\)-plane is also confirmed by this method. The changes of the axes are accompanied by strong changes of the bond distance of the apical oxygen ion to the Ni cation (Supplementary Fig. 7b). Remarkably, the calculated Ni–O distances agree well with the Ni–O distances from the Fast-ADT structural analysis (see Table 2). Further, the average bond distances are in excellent agreement with what would be expected from the sum of ionic radii for divalent (2.09 Å) and tetravalent Ni (1.88 Å).

The DFT calculations further predict fairly similar potentials for the redox couple La\textsubscript{2}NiO\textsubscript{4}/La\textsubscript{2}NiO\textsubscript{4}F\textsubscript{1} (\(0 \leq x \leq 2\)) independent on the exact values of \(x\) (Supplementary Fig. 7c). This potential is about 0.3–0.5 V higher than the potential of La\textsubscript{2}CoO\textsubscript{4}/La\textsubscript{2}CoO\textsubscript{4}F\textsubscript{1}\textsubscript{27,33}. This results in an increase of the energy density of La\textsubscript{2}NiO\textsubscript{4} compared to La\textsubscript{2}CoO\textsubscript{4}. La\textsubscript{2}SrMnO\textsubscript{4} in principle also allows for the insertion of approximately two fluoride ions per formula unit\textsuperscript{32,36}; however, the second fluoride ion can be only inserted at far higher potentials, which shows a severe destruction of the carbon additive, and makes this second plateau practically inaccessible for reversible battery applications (for a detailed discussion of the role of the carbon additive, see next section).

Determination of optimized charging conditions. To be able to optimize the cycling conditions of the cell, we aimed to gain a deeper understanding of the charging and discharging behavior by means of cyclic voltammetry (CV) and EIS.

The cyclic voltammograms for a La\textsubscript{2}NiO\textsubscript{4+x}/Zn–ZnF\textsubscript{2} cell show a broad peak at around 2.4 V, only in the forward direction of the first cycle, with a shoulder at lower potentials of around 1.8–2 V and a tail to as low as \(\sim 1\) V. The broad peak at 2.4 V corresponds to an irreversible anodic (side) reaction during the charging step (Fig. 4a), and in case of the occurrence of the irreversible anodic reaction, no cathodic peak can be observed in the backward direction. However, limiting the cycling potential range to 2 V (see Fig. 4a) results in the observation of a reversible cathodic peak at \(\sim 1\) V in the backward direction (see again Fig. 4a). A similar behavior is also observed when Pb–PbF\textsubscript{2} (see Fig. 4b) is used as the counter electrode (anode material), where the corresponding peaks occur at potentials reduced by ca. 0.4 V (the cathodic peak can be seen around \(\sim 0.6\) V for Pb–PbF\textsubscript{2}) due to the higher potential of this anode system compared to Zn–ZnF\textsubscript{2} (Fig. 4b). Unlike batteries that use a liquid electrolyte, it is not possible to construct a three-electrode set-up within the heated battery system used within this study. Therefore, CV experiments must be performed in such a way that the counter electrodes (anode materials) were used as reference electrodes. This explains the potential shifts observed for measurements against Zn–ZnF\textsubscript{2}.
in comparison to measurements against Pb-PbF₂ (the cyclic voltammograms basically coincide if corrected by the standard potential of M/MF₂ (M = Pb, Zn) derived from the formation energies given in ref. ⁹, see Supplementary Fig. 8). Since both, La₂NiO₄₊₁/₁₂/Pb-PbF₂ and La₂NiO₄₊₁/₁₂/Zn-ZnF₂ cells were cycled to 0 V as the lowest potential, this implies different degrees of de-fluorination after the first cycle. Therefore, different degrees of de-fluorination in combination with achieving identical CV conditions for both cells could explain the cathodic peak shift for the La₂NiO₄₊₁/₁₂/Zn-ZnF₂ cell (Fig. 4a) for higher cycles, which was not observed for the La₂NiO₄₊₁/₁₂/Pb-PbF₂ cell (Fig. 4b).

Further, the CNTs seem to be quite stable at potentials below ~1.3 V (against Pb-PbF₂ anode material; ~1.9 against Zn-ZnF₂) based on the difference (~0.6 V) in the standard potentials of Pb/ Pb²⁻ and Zn/Zn²⁺) according to the cyclic voltammogram of a pure carbon-based cathode (Supplementary Fig. 9). An irreversible anodic peak can also be observed at ~2.1 V in the cyclic voltammogram of C/Pb-PbF₂, which corresponds probably to carbon oxidation. It is worth noting that the observed irreversible anodic peak in the cyclic voltammogram of C/Pb-PbF₂ can also be observed in the cyclic voltammograms of La₂NiO₄₊₁/₁₂/Pb-PbF₂ and La₂NiO₄₊₁/₁₂/Zn-ZnF₂ cells (Fig. 4). Further, it can be assumed that the peak shifts toward the lower potential range shows the catalytic effect of the La₂NiO₄⁺₁/₁₂ compound for carbon oxidation⁴².

In order to have a better understanding on the nature of the irreversible anodic reactions on the carbon additive observed via CV, galvanostatic impedance spectroscopy has been performed for the La₂NiO₄₊₁/₁₂ cell against Zn-ZnF₂ (see Fig. 5a, b; similar behavior is observed for charging against Pb-PbF₂, see Supplementary Fig. 10a, b) during the first charging step. It can be seen that the Nyquist plots of the La₂NiO₄₊₁/₁₂/Zn-ZnF₂ cell at low charging capacities consist of a semicircle at high frequencies (>10 kHz) corresponding to the impedance of the solid electrolyte and interface resistance between the electrolyte and the electrode material²⁷ followed by a straight line with a slope of ~1 at frequencies <10 Hz arising from the diffusion processes within the active electrode materials⁴⁸, often referred to Warburg impedance⁴⁹ (Fig. 5b). This type of Nyquist plots are similar to what has been observed²⁷,³³ for La₃CoO₄ against conversion-based anodes. It is worth emphasizing that the semicircles corresponding to the solid electrolyte and interface resistances cannot be resolved, which can also be seen from the BODE plots shown in Supplementary Fig. 11. The model, which can be used for fitting the Nyquist curves for capacities below ~130 mAh/g (corresponds to ~2 V), are labeled as “Model 1” in Supplementary Fig. 10c and consist of an RC circuit in series with a constant phase element (CPE) to describe the solid electrolyte plus interface resistance as well as the diffusion of fluoride ions into the electrode materials, respectively. For charging capacities belonging to potentials higher than ~2.0 V (higher than ~130 mAh/g), the slope of the straight line at low frequencies increases rapidly once the potential of the cell increases sharply, which is indicative for the development of a capacitive behavior of the cell. Then a different fit model (labeled as “Model 2” in Supplementary Fig. 10c) needs to be used, which differs from the first model by the use of a second resistance R₂ in parallel to the CPE.

The changes of the exponent α of the CPE on proceeded charging is plotted in Fig. 5a, confirming the capacitive behavior on transition from region (II) to region (III), and in agreement with the CV studies. More explanations about the CPE can be found in Supplementary Notes. In fact, the values of the exponent α appears to be around 0.5 within region (II), which is indicative for a Warburg-type behavior, while the α values rapidly increase up to 0.8 at region (III). It also needs to be particularly emphasized that this behavior does not appear within region (II) and therefore cannot correspond to the partial decomposition of the active cathode material observed from the reduction of the Ruddlesden–Popper reflections by XRD.

To highlight the role of the carbon additive, we performed XPS measurements of the C1s emission line. On extended charging in region (III), additional broad high energy signals are appearing, in addition to a shift of the binding energy of the main sharp carbon signal by approximately 0.5 eV, which already occurs in region (II) (see Fig. 5c, d). This indicates an increasing oxidation (fluorination) of the carbon (or of a neighboring carbon atom)⁴⁰,⁵³. To visualize this oxidation, we represented the changes of carbon by a single parameter, which we calculated as the area-weighted average binding energy of each C1s emission line. This weighted binding energy increases strongly with increased charging (see Fig. 5d). The partial fits for all samples are shown in Supplementary Fig. 12 (details on the fitting procedure can also be found in Supplementary Notes together with additional partial spectra shown in Supplementary Fig. 13, which are dominated by the electrolyte and carbon signal).

The change of the carbon additive on charging is also reflected by using spectroscopical methods. The Raman spectra of pristine CNTs (before milling) and the samples before and after charging to 120 and 400 mAh/g can be found in Fig. 5e (the spectra were normalized to the maximum intensity of the D band in the respective spectrum). The observed bands are characteristic for carbonous materials. The G band is present in all graphene and graphitic materials and is originating from bond stretching of sp²-hybridized carbon atoms. Owing to the presence of defects and disorder (i.e., everything which would lower the crystalline symmetry of the quasi infinite graphene lattice), the D (D for defect) and D’ bands are observed. Second-order Raman scattering is found at higher Raman shifts.⁵² The formation of disorder (e.g., by defects induced during milling or in the form of oxidized C species on charging) is well represented by the changes in the integral intensity ratio of the D and G bands.⁵³,⁵⁴ As shown in Fig. 5f, additional disorder due to milling/charging leads to a considerable intensity increase of the D mode, while the intensity of the G band decreases. The highest I_D/I_G ratio was found for the sample charged to 400 mAh/g, which lies in region (III) and is therefore significantly overcharged, whereas at the end of region (II), the I_D/I_G ratio is more similar to the defect state, which was obtained after milling.

From the experiments performed, one can derive a more detailed picture on the potential-dependent structure and fluorine distribution on the CNTs. It is clear that the degree of oxidized (fluorinated) species increases within region (II) and (III); parts of the CNTs are already oxidized at potentials where the fluorination of La₂NiO₄⁺₁/₁₂ also takes place, i.e., within region (II), but within this range no strong increase in the impedance of the cell can be observed. At the transition to region (III) as well as within region (III), there seems to be a change in the principle impedance behavior of the cell (change from resistive to capacitive), which would imply that in this region the electrical conductivity of the CNT must be severely deteriorated. This can be correlated with previous studies: (1) Li et al.⁵⁵ have shown that fluorination starts at the defect sites of the CNT and then continues also to other sites. (2) Yue et al. have demonstrated that increasing degree of fluorination (increasing amount of defects) results in a strong decrease of the conductivity of CNT⁵⁶. This would be in principle agreement with the data recorded: Within region II, defect states of the CNT, which are induced to an even larger extent during the milling process, are likely to be fluorinated first; the electronegative fluoride ions at these former defect sites cause the change of the binding energy of the main sp² carbon signal due to their strong inductive effect. However, this would not result in a further decrease of conductivity, since
those defects had broken the sp² networks of the CNT already after milling. On increasing the degree of fluorination in region III (increase of oxidized carbon species), the sp² network of the CNT gets distorted even further by the fluorination of regular carbon sites or by affecting also the inner CNT, which would lead to an ongoing decrease of conductivity, hindering electron transfer to the active cathode material.

Clearly, the fact that the carbon matrix is changed in a side reaction on charging of the cells requires a fine-tuning of the charging and discharging conditions in order to establish reversible all-solid-state FIBs. We conclude that a reversible fluoride intercalation/deintercalation into/from La₂NiO₄ requires that the creation of further defect states within the CNT matrix has to be avoided, since the electronic conductivity of the carbon

Fig. 5 State of charge-dependent impedance study of La₂NiO₄⁺δ and the role of carbon nanotube additive. a Results of the galvanostatic electrochemical impedance spectroscopy and variations of α by charging of the electrochemical cells build up from La₂NiO₄⁺δ against Zn-ZnF₂ anode materials at an operational temperature of 170 °C; b respective Nyquist curves at different charging capacities for the La₂NiO₄⁺δ/Zn-ZnF₂ cell; c XPS measurements (background corrected) of the C1s emission line on the carbon nanotube before mixing/milling (CNT) and samples before charge (heated at 170 °C inside an Ar-filled glovebox for 6 h) and after charge at different cutoff capacities of 80, 150, and 400 mAh/g; d changes of the area-weighted average binding energy of the C1 emission versus charge capacity for CNT and the samples before (heated) and after charge; e) Raman shifts for the carbon nanotubes (before mixing/milling) and the cathode composite before and after charge up to 120 and 400 mAh/g; and f) corresponding I_D/I_G ratios obtained from the Raman shifts.
matrix would be lowered and the transfer of electronic charge carriers to the active cathode material would be impeded. This optimization of operation conditions is described in detail in the subsequent chapter.

In addition, it is again worth emphasizing that XPS cannot be used to track the changes of the Ni oxidation state or other changes in the Ruddlesden–Popper-type phase. This originates from the fact that the particles of the active material show a strong coverage with the electrolyte and/or carbon species (see TEM images given in Fig. 3a, b and Supplementary Fig. 1 and further information on the XPS studies provided in Supplementary Discussion). Therefore, no Nickel signal could be observed, showing that the XPS spectra provide only information on the nanocrystalline carbon and electrolyte additives.

On the structural reversibility of the fluorination of \( \text{La}_2\text{NiO}_4.13/\text{La}_2\text{NiO}_4.13\text{F}_{1.87} \). Figure 6a depicts a typical charge/discharge curve of a \( \text{La}_2\text{NiO}_4.13/\text{Zn-ZnF}_2 \) electrochemical cell charged to 120 mAh/g, which is discharged with a reduced discharging current of \(-2.4 \mu\text{A/cm}^2\) \((-1.0 \mu\text{A})\). A drop in the discharge potential of \(-0.4 \text{V}\) was found between the end of the charge and the beginning of the discharge. This “IR drop” is arising from the polarization coming from internal resistance (impedance) of the electrode materials\(^1,3\). The IR drop is followed by an extended sloping discharge plateau between \(-1.2\) and \(-0.8 \text{V}\). Such sloping plateaus are commonly found for layered cathode materials for LIBs\(^3\), indicating compositional flexibility of the various compounds. The discharge voltage plateau for the \( \text{La}_2\text{NiO}_4.13/\text{Zn-ZnF}_2 \) cell seems to be higher than the \( \text{La}_2\text{CoO}_4/\text{Zn-ZnF}_2 \) by approximately \(-0.4 \text{V}\), showing the higher energy density of this compound from the fact that the redox potential \( \text{Ni}^{2+/3+} \) is higher than the redox potential \( \text{Co}^{2+/3+} \). Finally, toward the end of the discharge process the potential drop between \(-0.8\) and \(-0.0 \text{V}\) occurs with an increasing slope.

The discharge capacity is measured to be around \( 70 \text{mAh/g} \) (Fig. 6a), which is the highest discharge capacity that has been obtained so far for an FIB with an intercalation-based cathode material (Supplementary Fig. 14 and Supplementary Table 7 summarize the discharge capacity of \( \text{La}_2\text{NiO}_4.13 \) as compared to the other previously studied intercalation-based cathode materials including \( \text{La}_2\text{CoO}_4 \), \( \text{LaSrMnO}_4 \), and Schafarzikite-type structure of \( \text{Co}_{0.5}\text{Fe}_{2.5}\text{Sb}_2\text{O}_6 \) showing the highest obtained discharge capacity for the \( \text{La}_2\text{NiO}_4.13/\text{Zn-ZnF}_2 \) electrochemical cell). Note that such a high discharge capacity can only be found by using small discharge current density such as \(-2.4 \mu\text{A/cm}^2\) \((-1.0 \mu\text{A})\). On using a higher discharge current density of \(-12 \mu\text{A/cm}^2\), the discharge capacity reduces to \(-50 \text{mAh/g} \) (see also Supplementary Fig. 15).

The XRD measurements show a complete disappearance of the fluorinated phase on discharging (Fig. 6b). Two phases with reduced c lattice parameter (and therefore cell volume) were found after discharging. The first phase (phase 1) is very similar to the original \( \text{La}_2\text{NiO}_4.13 \) before charge with similar cell volume \((V = 379.80(15) \text{ Å}^3)\) and a small orthorhombic distortion \((a = 5.4598(10) \text{ Å}, b = 5.5097(15) \text{ Å}, c = 12.6256(28) \text{ Å})\). The second phase shows a strong broadening of the (103) reflectation, and we used a Gaussian distribution of phases with c lattice parameters ranging between \(-12.81\) and \(-13.56 \text{Å}\) to fit this phase in the XRD pattern (which are given as a summed partial curve labeled as “phase 2” in Fig. 6b). The broad distribution of de-fluorinated phases is best explained with a small fluctuation of the strongly reduced fluoride content within this compound, in agreement with the sloping discharging plateau. After discharging, the molar ratio of phase 1 (\( \text{La}_2\text{NiO}_4.13 \)) to phase 2 (i.e., nearly unfluorinated to strongly de-fluorinated) is about 1:51 and clearly distinguishes from the ratio of 2:1 of fluorinated \( \text{La}_2\text{NiO}_4.13\text{F}_2 \) to unfluorinated \( \text{La}_2\text{NiO}_4.13 \) found after charging. This shows an excellent structural reversibility of the fluorination process for \( \text{La}_2\text{NiO}_4.13 \). Further, the low Coulombic efficiency of this first charge/discharge capacities cycle together with the reduction of the Ruddlesden–Popper phase content at higher charging capacities is in agreement with the side reactions of the oxidation (fluorination) of the defect states of the CNT as reported in the previous chapter. This does not significantly impair the conductivity of the cell below \(-2.2 \text{V}\) according to the impedance spectroscopic measurements (see Fig. 5a).

Developing a highly reversible all-solid-state FIB. Taking into account the findings of the previous sections, the cycling conditions of the \( \text{La}_2\text{NiO}_4.13/\text{Zn-ZnF}_2 \) cells were optimized in order to obtain stable cycling behavior. Therefore, two cutoff criteria were set for the charging reaction: (1) a cutoff voltage of \(-2.3 \text{V}\) was chosen as a result from the potential jump shown in Fig. 2a (after which the cell builds up additional resistances most severely due to increasing amount of defect states in the CNT network as found in the impedance study). (2) Different cutoff capacities of \(-30, 50, 80, \) and \(-120 \text{mAh/g} \) were then tested in order to find the optimized charging/discharging conditions of the cell (within the...
range where only already existing defects within the CNT network are impacted). Criterion (1) can only be met for samples with high cutoff capacities or at the highest cycling numbers of the cells with low cutoff capacities. For the latter, this originates from the charge efficiency slightly below 100% (98–99%, see Fig. 7), which result in a small but continuous degradation of the carbon additive. Figure 7 summarizes the electrochemical cycling behavior of the La$_2$NiO$_4$ cells with respect to the different cutoff charge capacities.

Clearly, the choice of the cutoff charging capacity can significantly influence the cycling behavior. For the lower cutoff capacities of 30 and 50 mAh/g, the discharging capacity increases continuously to 30 and 50 mAh/g during the first 5–10 cycles (see Fig. 7a, b, e). After those cycles, a Coulombic efficiency of on average 98–99% (average Coulombic efficiency for the whole cycling range: 97.68% and 95.44% for charge cutoff capacities of 30 and 50 mAh/g, respectively) is obtained (see Fig. 8). As discussed, the low Coulombic efficiency at the early cycle numbers originate from the presence of the side reactions on the carbon additives and show that the cells can be activated to become cycling stable by the more careful subsequent charging/discharging within the first cycles.

Interestingly, the phase behavior at extended cycling numbers is also different to what was observed for the first charging/discharging with a cutoff capacity of 120 mAh/g. At cycle number 10 (for the cell with cutoff capacity of 30 mAh/g), the XRD

Fig. 7 Cycling behavior of La$_2$NiO$_{4.13}$. Cycling curves of the La$_2$NiO$_{4.13}$/Zn-ZnF$_2$ at $T = 170$ °C, $I_{\text{charge}} = +24 \mu$A/cm$^2$, $I_{\text{discharge}} = -12 \mu$A/cm$^2$, and cutoff charge potential $= 2.3$ V at various cutoff capacities of a 30 mAh/g (for better depiction, only the first 80 cycles are shown), b 50 mAh/g, c 80 mAh/g, and d 120 mAh/g. e Variation of the discharge-specific capacity with cycle number for all of the mentioned cells.
measurements show that 2 high fluorine content phases with increased lattice parameter \( c \) (see Fig. 9a) coexist with a few other low fluorine content phases with slightly different lattice parameter \( c \) values. These phases are shown in Fig. 9a as a single average phase (phase 2).

Quantitative calculations based on the Rietveld method show that the summation (of the relative weight percent) of the high fluorine content phases (after charge up to 30 mAh/g) are about 36%; however, approximately 13% of those high fluorine content phases can still be found after the discharge (at tenth cycle) (Table 3). Therefore, ca. 23% of the active cathode material takes part in the redox reactions, which corresponds to accommodation of \( \sim 0.45 \) fluoride ions into the overall available \( \text{La}_2\text{NiO}_4.13 \) phase (which is the amount of fluoride ions corresponding to a specific capacity of 30 mAh/g for 100% Coulombic efficiency). The same argument is true for the cell with the cutoff capacity of 50 mAh/g after the sixth cycle: the summation of the relative fraction of the high fluorine content phases is around 45% of which ca. 8% retains after the discharge (Table 3), which shows participation of roughly 38% of the active cathode material in the redox reaction corresponding to an uptake of \( \sim 0.76 \) F\(^-\). Since a Coulombic efficiency of close to 100% (average Coulombic efficiency of 97.68% and 95.44% for charge cutoff capacities of 30 and 50 mAh/g, respectively) is found, this would mean that \( \text{La}_2\text{NiO}_4.13 \) would have to take up approximately two fluoride ions [(0.45/23%) \( \approx 2 \)], which is in agreement with the structural changes found from the structural and compositional analysis of the charged state by ADT, XAS, and EDX. In combination with the irreversibility of the side reaction of the carbon additives, we conclude that the charging and discharging capacities at higher cycle numbers can be fully assigned to the changes within the active cathode materials \( \text{La}_2\text{NiO}_4.13 \).

Therefore, it is important to note that the maximum capacity of \( \sim 100–120 \) mAh/g of the material can be fully accessed within the contributing particles: a limiting of the charging capacity does not result in a limited homogenous overall degree of fluorination, i.e., the grains do not change from a homogenous composition of the un-fluorinated state \( \text{La}_2\text{NiO}_4.13 \) to a homogenous composition of a partly fluorinated state \( \text{La}_2\text{NiO}_4.13\text{F}_{0.45} \). Instead, the presence of highly fluorinated phases \( \text{La}_2\text{NiO}_4.13\text{F}_{1.59} \) in addition to nearly un-fluorinated particles \( \text{La}_2\text{NiO}_4.13 \text{F}_d \) is observed experimentally. The smaller overpotentials, which can arise during the fluorination of the material, are the plausible origin why the carbon fluorination can proceed as a competing side reaction to some small extent (1–3%) at the higher cycle numbers. Without doubt, this undermines the high potential of the material to be improved further by, e.g., tailoring of the particle size/shape and/or coating of the surface in order to make the theoretical capacity fully accessible in future.

For the cutoff capacity of 30 mAh/g, the discharge capacity is highly stable at least over a range of 220 cycles with an excellent...
Coulombic efficiency for cycle numbers >10 (97.68% in average for the whole cycling range). However, after the cycle number 140, a small capacity loss can be observed followed by some discharge capacity fluctuations; we would like to acknowledge that until then the battery was already running for almost 3 months, and it is hard to trace back the detailed origin of this small capacity loss. For the cell with the cutoff capacity of 50 mAh/g, the discharge capacity is very stable up to the cycle number 40, again with high Coulombic efficiency (95.44% in average for the whole cycling range). After the 40th cycle (up to cycle number 60), the potential within the later stage of the charging reaches closer to the cutoff potential of 2.3 V (see Fig. 7b), which results in a complementary small reduction of the Coulombic efficiency (Fig. 8b). This is in agreement with the CV studies reported in the previous section, which show that the amounts of side reactions at the CNTs increases for increasing numbers of cycles. Based on this, we conclude that the slow and limited few cycles facilitating the maintenance of electrically conducting better separation of the La$_2$NiO$_4.13$/La$_2$NiO$_4.13$F$_{1.59}$ plateau from the discharge capacity (up to ~60 mAh/g for approximate 10 cycles).

By increasing the cutoff capacity to higher values of 80 and 120 mAh/g, the capacity fading on increased cycling is higher. From Fig. 7c–e, it can be seen that for the cell with the charge cutoff capacity of 80 mAh/g the discharge capacity increases up to ~46 mAh/g after 3 cycles; however, the cell experiences a severe capacity loss afterwards. For the cell with the higher charge cutoff capacity of 120 mAh/g, the first discharge capacity was approximately around 50 mAh/g; although this is the highest discharge capacity obtained for a cell based on an intercalation-based cathode so far (at a high discharge current density of ~12 µA/cm$^2$), the capacity loss is even more severe after 3 cycles, only 20% of initial discharge capacity could be recovered (Fig. 7d, e). This shows that a slow conditioning of the cells is preferable to improve their cycling behavior.

In addition, we would like to emphasize that contact loss from the active cathode material to electrolyte or carbon additives due to volume changes can also be an additional influence for capacity fading. Such influences could be previously resolved, e.g., for cathode materials for LIBs used with thiophosphate electrolytes, facilitated from the fact that such composites show a high density after compacting, which originates from the softness of the thiophosphate electrolytes. Attempts to analyze this aspect were also made for the La$_2$NiO$_4$ composite before and after charging to 120 mAh/g. However, in our case the composites are much more nanocrystalline, and La$_{0.9}$.Ba$_{0.1}$F$_{2.9}$ do not form a dense matrix around the active particles of La$_2$NiO$_4$$_{1.13}$ (overall density of ~70%, see scanning electron microscopic (SEM) images provided in Supplementary Fig. 18), which prohibits a detailed analysis of this aspect. This is also in full agreement with the TEM studies (see Fig. 3a, b and Supplementary Fig. 1), which could not provide detailed information on this aspect.

In summary, it is shown that by building all-solid-state FIBs based on Ruddlesden–Popper-type La$_2$NiO$_4$$_{1-d}$ as the cathode material, excellent cycling stability of such cells can be obtained. Detailed structural analysis of the single crystals (observed by STEM) of the charged/un-charged particles by means of Fast-ADT together with EDX and XAS measurements clearly show a change in the oxidation state of Ni and occupation of the anion.

### Table 3 Changes of phase fractions of the RP-type phases at different states of charge.

| Phase 1 (low fluorine content phase) [%] | Phase 2 (low fluorine content phase) [%] | Phase 3 (high fluorine content phase) [%] | Phase 4 (high fluorine content phase) [%] | Summation of low fluorine phases [%] | Summation of high fluorine phases [%] |
|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|------------------------------------|------------------------------------|
| 30 mAh/g after charge                  | 32.7 (±5)                              | 31.1 (±1)                              | 26.8 (±5)                              | 9.5 (±2)                           | 63.5 (±7)                           | 36.3 (±5)                           |
| 30 mAh/g after discharge               | 47.1 (±4)                              | 40.51 (±6)                             | 4.8 (±1)                               | 7.6 (±1)                           | 87.6 (±7)                           | 12.4 (±1)                           |
| 50 mAh/g after charge                  | 38.6 (±3)                              | 15.7 (±1)                              | 19.4 (±1)                              | 26.2 (±2)                           | 54.4 (±3)                           | 45.7 (±2)                           |
| 50 mAh/g after discharge               | 45.8 (±2)                              | 46.3 (±2)                              | 1.5 (±0.1)                             | 6.3 (±0.3)                          | 92.1 (±3)                           | 7.9 (±0.3)                           |

Relative fractions of the different phases of the La$_2$NiO$_4$$+(x)$ active cathode material after charge and discharge against Zn-ZnF$_2$ (at $T = 170$ °C, $i_{charge} = +24$ µA/cm$^2$, and $i_{discharge} = -12$ µA/cm$^2$) at the tenth and sixth cycle for the cutoff capacities of 30 and 50 mAh/g, respectively. Further details of the Rietveld refinement can be found in Supplementary Table 9.
interlayers of La$_2$NiO$_{4+d}$ by fluoride ions over electrochemical charge, revealing the origin of the charge/discharge curves. The results reveal that the cutoff criteria (cutoff charge capacity and voltage) play a vital role in the cycle life of the cell and that the formation of stable interfaces between the active material and especially carbon-based additives might play a similar role for cathode materials in FIBs than for anode materials in LiBs. Clearly, it would be important to develop strategies to increase the reversibly accessible capacity closer to the capacity of around 106 mAh/g for formation of La$_2$NiO$_{4.13}$F$_{1.59}$. This is a general problem for FIBs and known within the community also for testing new battery systems based on liquid electrolytes. Therefore, we think that (as for all-solid-state LiBs) coating techniques as well as an advanced engineering of the electrode composites could help to improve the La$_2$NiO$_{4+d}$ system further. However, the high amount of fluoride ions per transition metal incorp- orated into La$_2$NiO$_{4+d}$ highlights the importance of multivalent electrode materials for battery applications.

**Methods**

**Preparation of the electrodes and electrolyte materials.** Within this article, the terminology of the electrochemical cell components (anode and cathode material) is based on the role of the electrode on the discharge. All of the cell components including electrolyte, anode composite, and cathode composite have been synthesized via ball milling using ZrO$_2$ vials and balls. Note that the vial was filled and extracted at a high purity Ar-filled (99.999%) glovebox and sealed before each milling process. The milling processes were conducted in 10-min intervals with 20-min rest between each interval (to avoid excessive local increase in temperature). Preparation of the La$_0.9$Ba$_{0.1}$F$_{2.9}$ electrolyte composite: Preparation of the La$_0.9$Ba$_{0.1}$F$_{2.9}$ was done according to literature$^{66}$; stoichiometric ratios of BaF$_2$ (STREM Chemicals, 99%) and LaF$_3$ (STREM Chemicals, 99.9%) were milled for 12 h at a rotational speed of 600 RPM (runs per minute).

Preparation of the La$_2$NiO$_{4+d}$ cathode composite: For preparation of the La$_2$NiO$_{4+d}$ cathode composite material, first the pure La$_2$NiO$_{4.13}$ compound was synthesized by solid-state reactions according to previous reports$^{61,62}$. Stoichiometric ratios of La$_2$O$_3$ (Alfa Aesar, 99.9%, pre-dried at 120 °C for 12 h before cathode-type NiO (Sigma Aldrich, 99.99% re-dried at 700 °C for 12 h before use) were mixed and heated under air at 800 °C for 10 h. Then the mixture was hand-ground and re-heated under air at 1400 °C and kept for 4 h. The heating/cooling rates were 2 and 3 °C/min, respectively. For preparation of the La$_2$NiO$_{4+d}$ cathode composite, 30 wt % of the as-synthesized La$_2$NiO$_{4.13}$ was mixed with 60 wt % of the electrolyte (La$_0.9$Ba$_{0.1}$F$_{2.9}$) and 10 wt % of CNTs (dried at 190 °C under Ar) to improve the ionic and electronic conductivity of the cathode material (corresponding to volume fractions of 23 vol % La$_2$NiO$_{4.13}$, 52 vol % La$_0.9$Ba$_{0.1}$F$_{2.9}$, and 25 vol % CNTs). The mixture was then ball milled for 3 h at a rotational speed of 250 RPM. Note that higher milling speed would result in amorphization of the La$_2$NiO$_{4+d}$, destroying the layered structure which is a prerequisite for the structural reversibility of the intercalation of fluoride ions. The stability of La$_2$NiO$_{4.13}$ is well confirmed with respect to the absence of significant changes of the lattice parameters of the electrolyte and electrode material after this milling process and from the quantitative phase analysis of the electrode composite (Supplementary Table 1), which agrees well with the presence of La$_0.9$Ba$_{0.1}$F$_{2.9}$ and La$_2$NiO$_{4.13}$ in the weighted relative phase fractions. Further, it is worth mentioning that, after compacting, the electrode composites possess a relative porosity in the range of 50%, as described in our previous article$^{27}$.

Preparation of Zn-ZnF$_2$ anode composite: 50 wt % of the La$_0.9$Ba$_{0.1}$F$_{2.9}$ electrolyte material, 20 wt % of the Zn (Sigma Aldrich, >99%), 20 wt % of ZnF$_2$ (STREM Chemicals, 99%), and 10 wt % of black carbon (dried at 190 °C under Ar) were milled for 12 h at a rotational speed of 600 RPM.

Preparation of Pb-PbF$_2$ anode composite: 45 wt % of Pb (Sigma Aldrich, >99%), 45 wt % of PbF$_2$ (STREM Chemicals, 99%), and 10 wt % of dried black carbon were milled for 12 h at a rotational speed of 600 RPM.

**Electrochemical testing.** To make a battery cell, three layers of cathode/electrolyte/anode were pressed at a pressure of 2 tons for 90 s, using a desktop press (Specac) inside an Ar-filled (99.9999%) glovebox. The dimensions of the cell were measured to be 1.6 and 7.3 mm for the thickness and the diameter, respectively. Battery cells were spring-loaded (as described in ref. 27) into a modified air-tight Swagelok-type cell with current collectors made of stainless steel. All electrochemical cells were loaded, sealed, and removed in a high purity Ar (99.9999%) glovebox. However, for electrochemical testing, the sealed cells were operated outside the glovebox. To ensure sufficient mobility of the fluoride ions within the electrolyte, the electrochemical cells were heated at 170 °C. To minimize the thermal fluctuations (typical temperature drift of ≲0.1 °C), the electrochemical cells were kept with glass wool and the room was held at 21 °C by an air conditioner. We would like to emphasize that this operation temperature was already optimized in a previous study$^{28}$ at ambient temperature, the conductivity of the electrolyte is below 10$^{-6}$ S/cm, which implies an increase of the inner resistance by a factor of >100 and overpotentials >10 mV for the current densities chosen, so that no charging can be obtained within a potential range of 0–3 V. On the other hand, increasing the temperature to 200 °C was found to decrease the Coulomb efficiency by a factor of 3 within our previous study on La$_2$CoO$_{4+δ}$,33. Therefore, the operation temperatures of 170 °C can be considered as an optimized choice for the operation of this class of compounds.

Battery testing was performed using an potentiostat from BioLogic (SP-150 or VSP900). All voltages are given as potentials against the anode material. The mass of the active cathode material La$_2$NiO$_{4+d}$ was approximately 1.5 mg and anode composites were used in a 20-fold capacity excess compared to the active cathode material. In this respect, all specific capacities in this article are given with respect to the amount of the active cathode material. This composition is chosen in accordance with our experience on testing different composite compositions (an example can be found in Supplementary Fig. 19). Further, higher absolute masses result in easy delamination of the cathode side and were therefore not considered.

The electrochemical experiments were performed galvanostatically, with charging and discharging currents of +10 µA (cutoff charge) and a voltage cutoff (2.3 V) or a capacity cutoff (30, 50, 80, 120 mAh/g), depending on what was reached first. The voltage cutoff criterion was chosen based on results obtained from a CV study performed at 170 °C with a scan rate of 0.1 mV/s.

**Impedance spectroscopy.** EIS of the cells was performed simultaneously during the galvanostatic charging at 170 °C within the frequency range between 500 kHz and 0.1 Hz, using a Zahner IM6e electrochemical work station. Impedance spectra were recorded at different potentials (2.3 V at the start of the experiment) and a current density of 50 µA (cutoff charge) and a voltage cutoff (2.3 V) or a capacity cutoff (10 µA (~24 µA/cm$^2$)) and were performed with a total measurement time of 4 h using a step size of −0.0007 and a fixed time constant of 0.3 Ω. For high-resolution measurements, the counter electrode was kept constant; however, the angular range was reduced to 27°–36° 2θ.

Analyses of diffraction data were performed using the Rietveld method as implemented in TOPAS V5. The instrumental intensity distribution was determined empirically from a sort of fundamental parameters set using a reference scan of LaB$_6$ (NIST 660a). The microstructural parameters (crystallite size and strain) were refined to adjust the Rietveld refinement. Dispersion parameters were constrained to be the same for all atoms of all phases to minimize quantification errors and to account for angular-dependent intensity changes induced by absorption and surface roughness.

**X-ray absorption spectroscopy.** To obtain sufficient amount sample in a charged state, 5 cells were charged to 120 mAh/g. The cathode sides were carefully scratched off (inside the Ar-filled glovebox) and merged. La$_2$NiO$_{4.13}$ (0.030 ≤ d ≤ 0.17) standards (for XAS measurements) were produced by heating stoichiometric (of d) La$_2$O$_3$ and NiO at different atmospheres. For more detailed information concerning the XAS reference preparation, please see Supplementary Table 6 (respectively XRD patterns of the phases and their lattice parameters can be found in Supplementary Fig. 20 and Supplementary Table 1).

X-ray absorption experiments were carried out at beamline P65 at Deutsches Elektronen-Synchrotron Desy in Hamburg (Germany). For the measurements at the Ni $K$-edge at 8333 eV, a Si(111) double-crystal monochromator was applied in continuous scan mode (180°/spectrometer). Owing to the low Ni concentration of the samples, spectra were recorded in fluorescence geometry using a passivated implanted planar silicon (PIPS) detector. The preparation of the samples was carried out under inert atmosphere in a glove box producing pellets diluted with boron nitride. Monochromator calibration was carried out using a Ni foil. More detailed information about data analysis are given in Supplementary Information.

**Transmission electron microscopy.** TEM samples were prepared by placing a drop of the powders dispersed in n-hexane on a carbon-coated copper grid. The powder was evaporated in a vacuum oven at 60 °C to remove the solvent. A JEOL JEM F30 TWIN transmission electron microscope equipped with a field emission gun and operated at 300 kV was used. Ten-µm condenser aperture, spot size 6, and gun lens 7 were set to produce a quasi-parallel beam with a 200-nm size for the ADT experiments. In case of the EDX spectroscopic measurements, a 50-µm condenser aperture, spot size 6, and gun lens 7 were used to increase the electron dose and have a reliable amount of counts on the EDX detector (EDAX EDAM III). STEM images were collected using a Fischione HAADF detector. Electron diffraction patterns were
acquired with an UltraScan4000 CCD camera provided by Gatan (16-bit, 4096 × 4096 pixels). Hardware binning 2 and exposure time of 2 s were used to acquire non-saturated diffraction frames. ADT datasets were acquired with an automated acquisition module developed for FEI and JEOL microscopes, called hereby Fast-ADT, which allows the acquisition of electron diffraction tomographies in around 10 min for conventional CCD cameras and fixed tilt step of 1°45. Precision electron diffraction (PED)26 was coupled to the Fast-ADT data collection to minimize the dynamical effects and improve the reflection intensity integration quality.28 PED was generated by means of the DigitStar system developed by NanoMegas SPRIL and it was kept to 1°.

Three-dimensional processing of the Fast-ADT data was done by the eADT software package.29 Sit20145 was used for ab initio structure solution and Jana20065 was later used for crystal structure refinement. Intensity extraction for dynamical refinement was done by PETS.39 EDX peak identification and quantification was carried out by the ES Vision software.

**Scanning electron microscopy.** To investigate potential microstructural changes within the electrode composites, SEM images were recorded on cross-sections of the pellet with a Philips XL30-FE dual using a voltage of 30 kV. The samples were gold-coated for 40 s prior to SEM measurements.

**X-ray photoelectron spectroscopy.** The XPS measurements were performed by a Physical Electronic VersaProbe XPS unit with the PHI 5000 spectrometer analyzer. As the X-ray source, Al Kα radiation (1486.6 eV) with a power of 50.6 W was used. The step size and pass energy for the detailed spectra were set to 0.1 and 23.5 eV and for the survey spectra to 0.8 and 187.85 eV, respectively. As reference materials, gold and silver with the respective gold 4f7/2 (Ag3d5/2) emission line at 84.04 eV and the silver 3d5/2 (Ag3d5/2) emission line at 368.3 eV were measured, to correct the binding energy of the spectra by the characteristic shift of the instrument. In order rule out photocurrent-induced charging of the sample, the valence band, which is dominated by the stable electrolyte phase La2O3•CuF2, was measured. Since the valence band energies were identical for the different samples, no further corrections were necessary. Further, no sputtering was done prior to and during the measurement, as well as no neutralization was necessary. For the background correction, a Shirley-type correction was used. Note that prior to XPS measurement of the uncharged sample, this sample has been heated at 170 °C for 6 h inside an Ar-filled glovebox to be more in line with the actual charging conditions.

**Raman spectroscopy.** Charged pellets (at 120 and 400 mAh/g) were used for Raman spectroscopy. Raman spectra were recorded with a confocal micro-Raman spectrometer Horiba HR 800 equipped with a helium-neon laser with a wavelength of 633 nm. Integral intensities were fitted using Pseudo-Voigt functions.

**Density functional theory.** The quantum mechanical calculations were performed in the Vienna ab initio simulation package27, by employing the projector augmented wave method.28 The calculations were based on the use of pseudopotentials and of expansion of wave function in terms of the plane wave basis set. The kinetic energy cutoff for the latter was set equal to 600 eV. The reciprocal space was fitted using Pseudo-Voigt functions.

**Chemical fluorination.** Attempts on chemical fluorination of the La2NiO4F(x) has been done by different fluorinating agents: CuF2 has been used as the fluorinating agent according to literature.27 For that purpose, two separated boat-like crucibles (one was filled with CuF2 and the other one with La2NiO4F(x)) were placed close to each other in an air-tight tube furnace under a flow of O2 (0.1 SLM) and heated up at various temperatures from 200 to 350 °C for 48 h. Fluorine gas diluted with argon (10% F2 by volume) was also used as the fluorinating agent at different temperatures and reaction times, which are stated directly in the figure captions (see Supplementary Fig. 4).

**Data availability**

All relevant data are available from the authors on request.

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Author contributions
M.A.N.: writing the manuscript, performed and organized the main part of the study. Synthesis of the precursors, preparation of electrochemical cells and samples for further measurements, XRD measurements, electrochemical measurements (galvanostatic cycling, cyclic voltammetry, impedance spectroscopy, etc.), analysis of the data, and plotting of figures. K.W.: Raman spectroscopy, M.D.: XPS measurements and analysis of fluoride. A.N.: XAS measurements and analysis of the respective data. R.S. and M.B.: XANES measurements and analysis of the respective data. A.M.M. and J.R.: DFT calculations and respective discussions. S.I. and F.K.: chemical fluorination of $\La_{2-x}$Ni$_x$O$_4$ by F$_2$. O.C. designed the study and supervised the project, scientific contributor, and scientific proofing of the manuscript.
Competing interests
The authors declare no competing interests.

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