Short communication

# A novel intercalation cathode material for sodium-based batteries

Bruno Rousseau [a,b,c], Vladimir Timoshevskii [c], Normand Mousseau [a,b], Michel Côté [a,b], Karim Zaghib [c,*]

[a] Regroupement Québécois sur les Matériaux de Pointe (RQMP), Canada
[b] Département de physique, Université de Montréal, C.P. 6128, Succursale Centre-Ville, Montréal, Québec H2C 3J7, Canada
[c] Institut de Recherche d'Hydro-Québec (IREQ), 1800 Bd Lionel Boulet, Varennes, Québec J3X 1S1, Canada

## ARTICLE INFO

## ABSTRACT

We propose $NaFeZr_2F_{11}$ and $NaFeTi_2F_{11}$ as novel materials for Na intercalation cathodes. The average sodium intercalation voltage for these compounds is about 4.0 V from first principles computations. The origin of this large voltage for a nominal $Fe^{2+}/Fe^{3+}$ redox couple is proposed to be a combination of the fluorine "booster" effect, the inductive effect and the stiffness of the proposed structure upon desodiation.

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## 1. Introduction

The intermittent output from renewable energy sources such as solar or wind is a major hindrance to their widespread application. Many directions are currently being pursued to overcome this issue [1–3], but a practical and cost-effective technology to store energy from renewable sources that allow the decoupling of production and distribution is not yet available. Rechargeable batteries, such as Li-ion batteries, are one example of a technology to address the issue with energy storage. Given that lithium is expensive, however, there is a strong interest for non-lithium battery technology for large-scale stationary storage, where cost and reliability are more important than energy density by weight [4].

Many advances in cathode materials for secondary lithium batteries have been achieved by focusing on transition metal oxides as intercalation compounds [5]. Thus, it is natural to first consider substituting lithium with a low-cost alternative such as sodium. However, Na insertion is energetically less favorable than Li insertion in these structures, leading to lower voltages [6]. An operating voltage as close as possible to the upper stability limit of the electrolyte is desirable in order to maximize energy capacity: a strategy to circumvent the less favorable Na insertion is thus desirable.

One such strategy is to use fluorine instead of oxygen in the structure with the transition metal in the cathode. Indeed, fluorine can act as a "voltage booster" because it forms stronger ionic bonds with transition metals, thus lowering the energy of their antibonding d orbitals and increasing the overall voltage [7]. Although some interesting structures

containing fluorine and oxygen have been studied [5], as well as the effect of partial substitution of oxygen with fluorine [7], few fluorine-only structures have been proposed so far [8,9]. Since oxygen and fluorine are not isoelectronic, simple substitution of O with F in successful oxide structures is not possible: new structures are needed.

In this work, the average Na insertion voltages for compounds $NaZr_2MF_{11}$, for M in (Fe, Ni, Co, Mn, Zr) are computed with emphasis on the iron-based structure. These compounds are known to exist experimentally [10] and adopt the structure presented in Fig. 1. Substitutions of Zr by other valence 4 elements are also considered in order to evaluate the impact of the "inductive effect" on the resulting voltage, with further emphasis on Ti as a likely and abundant substitute for Zr. Finally, we propose $NaZr_2FeF_{11}$ [10] and $NaTi_2FeF_{11}$ as new, fluorine-based cathode materials for sodium batteries.

## 2. Methodology

Voltages were computed by comparing total energies of completely sodiated and desodiated structures [6,11]. Computations were first performed at the level of density functional theory within the generalized gradient approximation (GGA, PBE functional [12]) using the Vienna ab initio simulation package (VASP) [13]. Some selected structures were also studied at the level of GGA + U [14–16], which partially corrects for the shortcomings of the GGA. The PAW formalism was used with high quality pseudopotentials [17,18]. All computations were performed with an energy cutoff of 520 eV and $4 \times 4 \times 4$ Monkhorst–Pack grids. The structures were relaxed until the largest residual force was smaller than 0.02 eV/Å.

Molecular dynamics simulations were conducted to assess the stability of the desodiated structures. We used the Siesta program package [19], which uses norm-conserving pseudopotentials and an efficient

* Corresponding author. Fax: +1 450 652 8424.
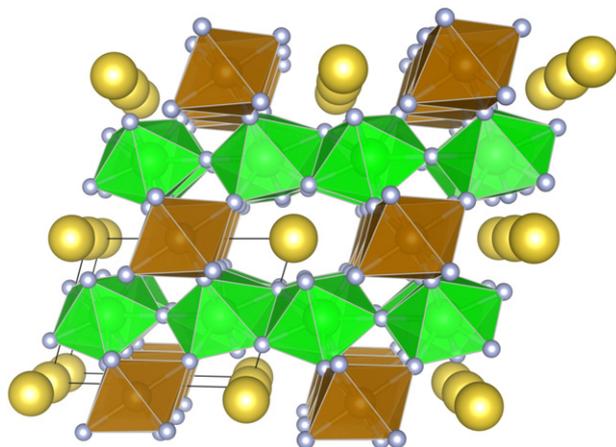  E-mail address: zaghib.karim@ireq.ca (K. Zaghib).

**Fig. 1.** Crystal structure of $NaZr_2FeF_{11}$. The sodium ions are represented by large yellow spheres and the fluorine by small gray spheres. The iron ions are located at the center of the octahedra formed by their fluorine near neighbors (brown polyhedra), whereas zirconium has seven fluorine near neighbors (green polyhedra).

localized basis set. The simulations were performed at constant volume and temperature (T = 333 K), using a time step of 1 fs. The total simulation period was 9 ps, which was preceded by a 2 ps period of thermal equilibration.

## 3. Results and discussion

The average voltages and volume changes upon full desodiation obtained in the GGA approximation for Fe, Ni, Co, Mn and Zn are presented in Table 1. The predicted voltages are either very close to the limit or too high to be sustained by current electrolytes for all transition metals except iron [20]; thus the Fe-based structure was singled out for further studies.

The voltage of the $NaZr_2FeF_{11}$ structure as well as the hypothetical substitution compound $NaTi_2FeF_{11}$ were computed using the GGA + U formalism. We adopt the value of U = 4 eV for Fe [21]; it is possible in principle to compute the value of the U parameter [16,21], but this goes beyond the scope of this work. Voltages were obtained by fully relaxing structures either within the GGA or the GGA + U. As a test, voltages were computed for various values of U between 2 eV and 6 eV: the voltage dependence on U is linear in this range, and varies by at most ± 0.2 V with respect to the U = 4 eV value, indicating that our results are robust and depend weakly on U.

The relaxed desodiated structures are very similar to the sodiated structures, with a small volume change as noted in Table 1. It is noteworthy that the distances between iron and its six neighboring fluorine ions go from 2.05 Å (2 ions) and 2.14 Å (4 ions) in $NaZr_2FeF_{11}$ to 1.97 Å

**Table 2**
Computed average voltages upon desodiation for $NaM_2FeF_{11}$, for M a tetravalent element, computed within GGA + U. The sodiated and desodiated structures are imposed to be the fully relaxed $NaZr_2FeF_{11}$ and $Zr_2FeF_{11}$ structures.

| M | IV-B family | | | IV-A family | | | |
|---|---|---|---|---|---|---|---|
| | Ti | Zr | Hf | Si | Ge | Sn | Pb |
| Voltage (V) | 4.1 | 4.0 | 4.1 | 4.5 | 4.6 | 4.4 | 4.4 |

(6 ions) in $Zr_2FeF_{11}$ (the Ti-based material displays similar behavior), which can readily be understood in terms of crystal field theory. Indeed, as Fe goes from 2 + to 3 +, five electrons are left to fully fill the spin polarized $t_{2g}$ and $e_g$ orbitals, with no possible energy gain from a Peierl's distortion. The results, presented in Table 1, indicate a remarkably high voltage of ~4.0 V using the redox couple $Fe^{2+}/Fe^{3+}$. This large value is of course partially explained by the fact that the iron atoms occupy octahedral sites with fluorine as near neighbor and fluorine yields stronger ionic bonds than oxygen. This is not sufficient to fully explain this high voltage, however, as this property is also shared by the $NaFeF_3$ structure, where the average voltage is predicted to be 2.7 V [9], in agreement with experimental measurements [8] (our own computations yield voltages of 3 V when comparing the sodiated structure to the $FeF_3$ polymorphs of symmetry Pnma, Pm-3m and R-3c).

Contrary to the $NaFeF_3$ structure, in the $NaZr_2FeF_{11}$ structure every fluorine is corner-shared between iron and zirconium, inducing charge transfer away from the iron site and increasing the voltage by the "inductive effect" [22]. This is illustrated qualitatively by computing the voltage of $NaM_2FeF_{11}$, for M a tetravalent element, keeping the structures fixed to the relaxed Zr-based structures. It should be noted that for M ∈ (Zr, Ti) these voltages may not be representative of the true value in these compounds (if indeed they exist and adopt this structure), as the structures were not allowed to relax. As can be seen in Table 2, the voltages thus obtained are roughly constant within the IV-A or IV-B family, but significantly larger in the IV-A family than in the IV-B, following the same trend as these elements' electronegativity, a feature also observed in simulations of polyoxianionic materials [23].

The volume change between $NaZr_2FeF_{11}$ and $Zr_2FeF_{11}$ is only about 6%, compared to about 16% for $NaFeF_3/FeF_3$(Pnma polymorph). If the desodiated structure is artificially forced to be identical to the sodiated structure with the Na removed (namely, if we prohibit relaxation), the voltages are given by 5.0 V ($NaZr_2FeF_{11}$) and 3.7 V ($NaFeF_3$); upon relaxation of the desodiated structures, these voltages are reduced by −1 V and −0.7 V respectively. Thus, structural relaxation has a significant effect on the average voltage, but cannot alone explain the important voltage differences between $NaZr_2FeF_{11}$ and $NaFeF_3$.

To assess the stability of the proposed structures, we considered their excess energy with respect to possible decompositions. As can be seen in Table 3, we find that $NaFeZr_2F_{11}$ is lower in energy by about 60 meV per atom than the considered decomposition products, in agreement with the fact that this compound is known to exist experimentally [10]. We also find that $NaFeTi_2F_{11}$ is lower in

**Table 1**
Computed average voltages and volume change upon desodiation for $NaM_2M'F_{11}$, where M ∈ (Zr, Ti) and M' ∈ (Fe, Ni, Co, Mn, Zn), computed within GGA and GGA + U for the Fe-based structures. The volume change is essentially the same for GGA and GGA + U.

| M | M′ | Voltage (V) | | ΔV (%) |
|---|---|---|---|---|
| | | GGA | GGA + U | |
| Zr | Fe | 3.6 | 4.0 | 6 |
| | Ni | 5.7 | – | 5 |
| | Co | 4.9 | – | 5 |
| | Mn | 4.4 | – | 9 |
| | Zn | 7.1 | – | 3 |
| Ti | Fe | 3.8 | 4.0 | 6–8 |

**Table 3**
Computed excess energy for the various materials considered with respect to possible stoichiometric decomposition (a negative excess energy indicates thermodynamical stability). Data from the literature [24] is also presented for delithiated $LiFePO_4$ (LFP) and $LiMn_2O_4$ (LMO) for comparison.

| Compound | Decomposition | Excess energy (meV/atom) |
|---|---|---|
| $NaFeZr_2F_{11}$ | $(NaFeF_3) + 2(ZrF_4)$ | −60 |
| $NaFeTi_2F_{11}$ | $(NaTiF_3) + 2(TiF_4)$ | −25 |
| $FeZr_2F_{11}$ | $(FeF_3) + 2(ZrF_4)$ | 10 |
| $FeTi_2F_{11}$ | $(FeF_3) + 2(TiF_4)$ | 40 |
| $FePO_4$ | $FePO_4$ (Pn2₁a polymorph) | 18 |
| $Mn_2O_4$ | $Mn_2O_4$ (I4/m polymorph) | 32 |

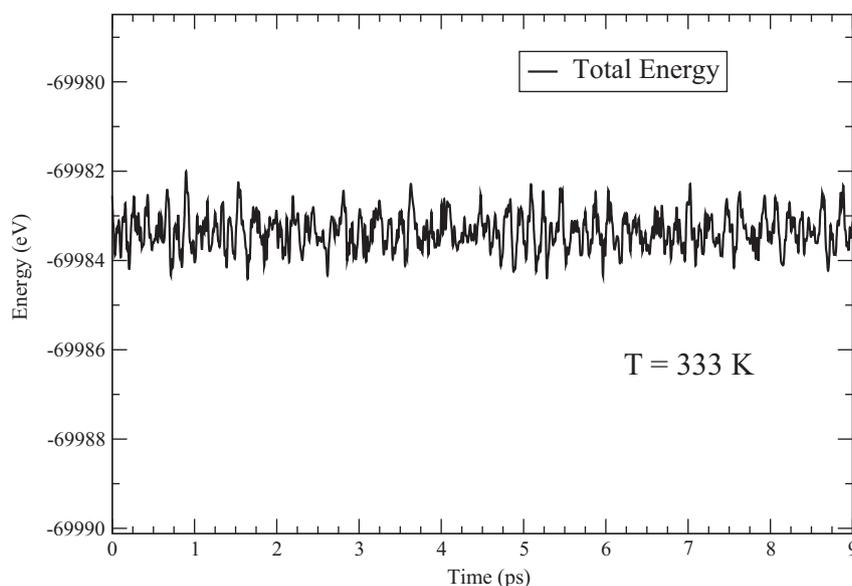**Fig. 2.** Total energy of the $FeZr_2F_{11}$ structure as a function of simulation time.

energy by about 25 meV per atom than the considered decomposition products.

We find that the desodiated compounds have excess energies per atom of approximately 10 meV ($Zr_2FeF_{11}$) and 40 meV ($Ti_2FeF_{11}$) compared to the decomposition products considered. It is not unusual for desodiated (or delithiated) cathode materials to be metastable energetically: for instance, the commercially successful material $LiFePO_4$, delithiated to $FePO_4$ in the olivine structure, is computed to have an excess energy of 18 meV per atom [24]. Similarly, the spinel $LiMn_2O_4$, delithiated to $Mn_2O_4$, exhibits an excess energy of 32 meV per atom [24]. The proposed desodiated materials exhibit similar excess energies to those well established materials.

To properly quantify kinetic stability, we conducted molecular dynamics simulations at finite temperature for the desodiated materials, for a time corresponding to hundreds of ionic vibration periods. The calculations demonstrated significant phonon vibrations in the heated system with the amplitudes of up to 0.3 Å from zero-temperature equilibrium positions, but the whole structure remained stable during whole simulation period. This can be seen in Fig. 2 for $FeZr_2F_{11}$ ($FeTi_2F_{11}$ displays similar behavior), which shows the evolution of the total energy of the system as a function of time. The total energy oscillates near the mean value, which does not change with time. This shows the absence of possible phase transitions in the structure during the simulation period.

## 4. Conclusion

In this work, we propose $NaZr_2FeF_{11}$ and $NaTi_2FeF_{11}$ as new cathode materials for secondary sodium batteries. The computed average voltages are about 4.0 V, which is optimal to take advantage of the best available electrolytes, and molecular dynamics simulations indicate that the desodiated structures are metastable. Furthermore, the sodium ions are arranged in wide channels in the structure, suggesting that ionic conductivity could be high. These promising cathode materials are composed of abundant elements, which may be economically advantageous. Finally, the relatively low theoretical capacity of these structures (~60 mAh/g) is not a major problem for stationary energy storage.

Efforts are currently under way to synthesize and characterize these structures. Further computational work is also being pursued to evaluate the most likely defects and compute the ionic conductivity.

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