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AUTHOR(S):
Shishkin, Maxim; Sato, Hirofumi

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Evaluation of redox potentials of cathode materials of alkali-ion batteries using extended DFT+U+U↑↓ method: The role of interactions between the electrons with opposite spins

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M. Shishkin1,a) and H. Sato1,2,3

AFFILIATIONS
1 Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan
2 Department of Molecular Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
3 Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto, Japan

a) Author to whom correspondence should be addressed: shishkin@riron.moleng.kyoto-u.ac.jp

ABSTRACT

Limitations of the DFT+U approach (e.g., in Dudarev’s formulation) applied for accurate evaluation of redox potentials of cathode materials of alkali-ion batteries with U parameters calculated via the linear response (LR) method are discussed. In contrast to our previous studies, where redox potentials of several cathode materials have been calculated in a good agreement with experiment (e.g., NaMnO2, LiFePO4, and LiTiS2), herein, we analyze other cathode materials, such as LiNiO2 and Ni- and V-containing phosphates for which this method provides much underestimated redox voltages. We ascribe this limited predictive power of the DFT+U method, parameterized via LR, to the absence of corrections of Coulomb interactions between the electrons with opposite spins. Using the recently proposed extended DFT+U+U↑↓ functional, which includes the aforementioned corrections, we show how redox potentials of Ni- and V-based compounds could be calculated in a much better agreement with experiment, also proposing a procedure of parameterization of such calculations. Thus, our extended method allows us to calculate redox potentials of several important materials more accurately while retaining good agreement with experiment for structures where the standard DFT+U method also accurately predicts electrochemical properties.

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I. INTRODUCTION

Accurate computational evaluation of redox potentials of electrochemically active materials is a challenging task, which requires solution for further development of Li-, Na-, and K-ion batteries as well as for fundamental understanding of electrochemical reactions. A simple expression is usually employed for the evaluation of redox potentials,1

\[ \Phi_r = \frac{E(x_1) - E(x_2) = (x_1 - x_2)E(Li)}{e(x_1 - x_2)} \quad (x_1 > x_2), \]  

(1)

where \( E(x_1) \) and \( E(x_2) \) are the energies of a cathode material with respective charge carrier concentrations \( x_1 \) and \( x_2 \), \( e \) is the charge of an electron, and \( E(Li) \) is the energy of a charge carrier cation (we use \( Li \) as an example). The important requirement that should be satisfied when applying Eq. (1) is a high accuracy of calculated differences \( [E(x_1) - E(x_2)] \), providing good agreement with the experimentally measured voltages. It should be noted that accurate calculation of energy differences is a difficult and long-standing problem in materials science, present in other important tasks such as the evaluation of formation energies or energies of chemical reactions.2

As local density functional theory (DFT) functionals are known to seriously compromise on the accuracy of computed potentials (or voltages) using Eq. (1),3 the Hubbard corrected DFT approach, so-called DFT+U framework, is often employed as a solution, which, in principle, could provide higher accuracy, using properly chosen values of \( U \) parameters.4–6 Moreover, low computational cost of DFT+U calculations, which is only slightly higher than local...
DFT, makes this method very attractive in contrast to other more time consuming although potentially very accurate techniques, such as hybrid functionals or quantum Monte Carlo method, recently tested for calculations of a voltage profile of LiNiO$_2$.

One of the difficulties, associated with application of DFT+$U$ approach, is the choice of a value of the employed $U$ parameter. The values of $U$ are usually chosen using empirical fitting of some observable quantity (e.g., energy of formation or materials bandgap) to the experiment. This approach has several limitations associated with the paucity of data on observable properties of materials. Another important aspect is the absence of universality of a prediction: accurate evaluation of one property (e.g., bandgap) for which the $U$ parameter has been adjusted, does not guarantee accurate evaluation of the other (e.g., redox voltage).

An attractive alternative to empirical search for the values of $U$ parameters could be their computational evaluation. Various methods have been proposed for this purpose, but we wish to highlight particularly the linear response (LR) evaluation of $U$ in view of its low computational cost and conceptual simplicity. The first application of LR parameterization of DFT+$U$ calculations to analysis of redox properties of cathode materials dates back to 2004. In that study, an averaged value of the $U$ parameter has been used for the evaluation of energies in Eq. (1) for each material in intercalated and deintercalated forms. More recently, we have demonstrated that LR coupled with DFT+$U$ calculations could provide very accurate values of redox voltages for several cathode materials, adopting respective calculated values of $U$ for intercalated and deintercalated cases. It should be noted that even this initial study exposed limits of DFT+$U$ method, where a very underestimated average potential has been predicted. In our subsequent work, we have also shown that DFT+$U$/LR method provides very underestimated redox potentials for the entire set of Fe sulfite cathode materials.

These tests not only exposed possible deficiency of LR parameterization of DFT+$U$ calculations but also questioned adequacy of DFT+$U$ framework itself, including its ability to provide accurate predictions of redox properties of the studied cathode materials. As a possible solution, we have re-formulated the form of Hubbard corrections, originally proposed by Dudarev and co-workers, by introducing an additional term that provides corrections for interactions between the electrons with opposite spins. Indeed, as we discuss below in a greater detail, the approach of Dudarev allows corrections for interactions between the electrons with the same spin only, whereas interactions between the electrons with opposite spins are treated using the local DFT functional and no respective corrections are applied. Our recent study has demonstrated that redox and magnetic properties of Fe sulfates can be calculated in much better agreement with the experimental reports if these additional corrections are included.

In this work, we discuss several cathode materials, where the DFT+$U$/LR approach provides very inaccurate (underestimated) redox potentials, as in the case of aforementioned LiNiO$_2$. We show that similar underestimation of the theoretical redox potential takes place for Ni phosphate–diphosphate and V-based organic phosphates. We discuss the deficiency of the employed DFT+$U$ framework and present a possible solution, applying the extended DFT+$U$+$U_{1f}$ functional. We also provide explanations as to why additional corrections are not necessary for several previously studied materials, reasonably described by Dudarev's form of Hubbard corrections.

II. THEORETICAL FRAMEWORK

A. DFT+$U$+$U_{1f}$ functional

Hubbard corrections are added to DFT energy, forming a DFT+$U$ expression, defined as

$$ E_{\text{DFT}+U} = E_{\text{DFT}} + E_{\text{Hub.}} - E_{\text{dec}}. $$

In addition to DFT and Hubbard energies ($E_{\text{DFT}}$ and $E_{\text{Hub.}}$ respectively), the double counting correction ($dcc$) is also introduced to remove those electron–electron interactions, which are present in both DFT and Hubbard terms. In the widely used approximation of Dudarev et al., which we also employ herein as a starting point, the combined Hubbard and $dcc$ term has the following form:

$$ E_{U} = \frac{U}{2} \sum_{\sigma} \sum_{n} n_{n}(1-n_{n}). $$

$U$ in Eq. (3) is a Hubbard parameter, technically equal to the difference between Coulomb and exchange coefficients $U - J$, which we simply denote as $U$. $n_{n}$ are the occupancy matrices, whose elements are calculated as

$$ n_{m\sigma} = \sum_{k\nu} \langle \psi_{k\nu}^{m}|P_{m\sigma}^{n}\psi_{k\nu}^{n}\rangle. $$

$P$ in Eq. (4) is a projector operator applied to electronic bands $|\psi_{k\nu}^{m}\rangle$ with weights $f_{k\nu}^{m}$ for projection on localized spherical harmonics ($\phi_{m}$ and $\phi_{n}$) centered on the atomic site,

$$ P_{m\sigma}^{n} = |\phi_{m}\rangle\langle \phi_{n}|. $$

Expression (3) limits the correction of electron–electron (electrostatic) interactions only to the electrons with the same spin, whereas corrections of interactions between the electrons with opposite spins are fully removed by the chosen form of double counting corrections in the method of Dudarev et al. [in Ref. 19, we have shown that the difference $E_{\text{Hub.}} - E_{\text{dec}}$ as in Eq. (2) is equal to zero for interactions between the electrons with opposite spins in the derivation of Eq. (3)].

Recently, we have proposed an extension of the correction functional, adding corrections for interactions between the electrons with opposite spins,

$$ E_{U+U_{1f}} = \frac{U}{2} \sum_{\sigma} \sum_{n} n_{n}(1-n_{n}) $$

$$ + \frac{U_{1f}}{2} \left( \sum_{\sigma} \sum_{\mu} \sum_{\nu} \sum_{\sigma'} \sum_{\sigma''} \sum_{n_{\sigma} n_{\sigma'}} |n_{\nu\sigma'} - n_{\nu\sigma''}| - \text{Tr}[N]|\text{Tr}[M]| \right). $$

The additional correction [second line in Eq. (6)] is presented as a trace of multiplication of occupancy matrices of electrons with opposite spins. Moreover, the additional linear terms in Eq. (6) dependent on the total density and magnetization ($N$ and $M$, respectively) are also introduced to account for $dcc$ due to this additional correction. The discussed additional term in Eq. (6) is multiplied by a coefficient $U_{1f}$. This choice of notation stems from the electrostatic type of interactions between the electrons with opposite spins, similar to a more common $U$ parameter, used for the parameterization of...
electrostatic interactions between the electrons with the same spin. In view of different magnitudes of these electrostatic corrections, two distinctive parameters are introduced in Eq. (6).

In our recent work, we have also presented the form of a Hamiltonian derived from the expression of the functional in Eq. (6), which allows us to carry out calculations with new introduced corrections of the interactions between the electrons with opposite spins.\(^1\)

We need to note that similar to the method of Dudarev et al.,\(^2\) the method of Liechtenstein et al.\(^3\) also does not provide corrections of interactions between the electrons with opposite spins despite a formal presence of the respective Hubbard term [as in Eq. (2)]. In Ref. 19, we have shown that both methods provide nearly identical description of the electronic structure due to the removal of introduced Hubbard corrections of discussed interactions by the chosen type of dcc (assuming the absence of exchange interactions).\(^4\) On the contrary, the second line of Eq. (6) is obtained via choosing dcc in such a way that they fully cancel respective Hubbard term only in the full localization limit, similar to other terms in the first line of Eq. (6) [see Ref. 19 for details, particularly Eq. (A4), which provides a modified expression for dcc].

The method of Liechtenstein differs from Dudarev’s formulation by the treatment of exchange interactions, which are, however, related to the electrons with the same spins. As we discuss in Sec. II B, our interest is focused on interactions between the electrons with opposite spins and therefore the method of Liechtenstein is also not a solution of the problems addressed herein. In Appendix A, we provide a comparison between the performance of the method of Liechtenstein et al. and Dudarev et al., as well as Eq. (6).

B. Materials classification and the strategy of evaluation of \(U_{11}\) parameters

Of particular interest in this study are the cathode materials, whose redox properties are calculated very inaccurately using a standard DFT+U method parameterized by the linear response method. A possible reason of this poor performance of the DFT+U method is the absence of corrections of interactions between the electrons with opposite spins. This deficiency of computational description could be very pronounced for structures, where d-electrons with opposite spins. This deficiency of computational method is the absence of corrections of interactions between the electrons with opposite spins.\(^5\)

The method of Liechtenstein differs from Dudarev’s formulation by the treatment of exchange interactions, which are, however, related to the electrons with the same spins. As we discuss in Sec. II B, our interest is focused on interactions between the electrons with opposite spins and therefore the method of Liechtenstein is also not a solution of the problems addressed herein. In Appendix A, we provide a comparison between the performance of the method of Liechtenstein et al. and Dudarev et al., as well as Eq. (6).

(i.e., interactions between the electrons with the same and opposite spins) have the same form. Therefore, both types of contributions are identical, including their double counting corrections. This property is very important and it confirms a very reasonable choice of double counting corrections, adopted in Eq. (6), as illustrated for the material with identical majority and minority channels, such as NiO.\(^6\) In passing, we need to note that suggestions of lifting dcc in the additional term in Eq. (6) (e.g., Ref. 21) do not seem justifiable, leading to the unphysical absence of dcc for one type of interactions (electrons with opposite spins) despite the presence of these for other types of interactions (electrons with the same spin).

We wish to elaborate on the role of interactions between the electrons with opposite spins further. The presented example of NiO provides an extreme case where the PDOS and hence the charges in two spin channels are identical. However, the ratio of charges in minority and majority channels \((N_{-\sigma}/N_\sigma)\) respectively might be different: \(N_{-\sigma}/N_\sigma\) could change from 0 to 1 if we assume for illustration purposes that \(N_{-\sigma} \leq N_\sigma\) (positive magnetic moment). The examples of materials with various values of \(N_{-\sigma}/N_\sigma\) are shown in Fig. 2, as could be clearly seen from the respective PDOSs of d-states.

Based on these observations, in Sec. IV, we provide the results of our calculations, classifying the studied materials into several groups using the ratio \(N_{-\sigma}/N_\sigma\) as a descriptor. In the first group, we discuss three materials, where the electronic charges of d-states in majority and minority channels are very substantial, leading to a relatively large value of \(N_{-\sigma}/N_\sigma\). These are LiNiO, K\(_2\)(VO\(_2\)PO\(_4\))\(_2\)(C\(_2\)O\(_4\))\(_2\), and Na\(_2\)Ni\(_3\)(PO\(_4\))\(_3\)P\(_2\)O\(_5\) materials (Subsection IV A, the PDOS of LiNiO is presented in Fig. 2, left). Then, we
proceed to the analysis of structures, where values of $N^{-\sigma}/N_{\sigma}$ adopt smaller (intermediate) values, i.e., two materials with LiVPO$_4$ F stoichiometry and LiFePO$_4$ (Subsection IV B, the PDOS of LiVPO$_4$ F is presented in Fig. 2, middle). In the Subsection IV C, we discuss a structure where the charge of one of the spin channels is significantly lower than the other (NaMnO$_2$: the PDOS is presented in Fig. 2, right) with the lowest value of $N^{-\sigma}/N_{\sigma}$. For this material, a standard DFT+U approach, parameterized by LR method provides reasonably accurate redox voltages as expected (Subsection IV C). Finally, we also add an additional group of structures (Subsection IV D), which are well described by the standard DFT+U approach, although large charges are present in both spin channels (LiCoO$_2$, LiTiS$_2$, and NaCuO$_2$).

Analysis of charges in spin channels could also be used for the estimation of values of parameters $U_{11}$. However, we employ other closely related quantities, namely, occupancy matrices ($n_{\sigma}$ and $n_{-\sigma}$) for this purpose. In order to adopt a certain value of the $U_{11}$ parameter, we propose the following expression using the value of $U$ parameter, obtained via LR approach,

$$U_{11} = -U \ast \frac{\sum_{\sigma} \text{Tr}(n_{\sigma} n_{-\sigma})}{\sum_{\sigma} \text{Tr}(n_{\sigma} n_{\sigma})} = -U \ast R.$$  

(7)

It is clear that in extreme cases, when the charge in one of the spin channels is either absent or charges in both channels are identical, $U_{11}$ is equal to zero or $-U$, respectively, according to Eq. (7). Moreover, Eq. (7) allows us to interpolate possible values of $U_{11}$ for more general intermediate values of a ratio of charges in two spin channels (parameter $R$). Additionally, based on our observation of calculation of redox potentials, we also choose to use an averaged coefficient $R$ in Eq. (7) for both intercalated and deintercalated structures, whereas $U$ parameters are evaluated self-consistently using the LR procedure.

We should note that for these tests, we tried to select materials for which evaluation of the average redox voltage could be meaningful in view of satisfaction of several requirements: (1) the voltage dependence from charge concentration should be close to linear and possibly constant, (2) it is desirable that complete or nearly complete deintercalation of studied structures should be possible [this allows obvious determination of both structures in Eq. (1)], and (3) only the cathodes with one type of TM are studied (we plan to analyze more complicated multi-cationic materials in future works). Additionally, we also targeted materials that could be used potentially as cathodes with attractive characteristics, such as a high operating voltage and acceptable durability for cycling.

III. COMPUTATIONAL DETAILS

The VASP package has been employed for all DFT+U calculations as well as calculations with the extended functional in Eq. (6). For the treatment of exchange correlation effects, we have used the Perdew-Burke-Ernzerhof (PBE) functional. Linear response calculations have been applied for the evaluation of $U$ parameters using the self-consistent procedure. $U_{11}$ parameters have been evaluated using Eq. (7) from Sec. II B. The Projector augmented wave (PAW) approach has been applied for the description of interactions between the electrons with atomic nuclei. The wave functions have been expanded into plane waves with a cutoff energy of 600 eV. The Monkhorst–Pack $k$-point mesh has been employed for the integration of the Brillouin zone. All studied cells have been fully optimized, including their lattice vectors and atomic positions of all atoms until the maximum atomic force dropped below 0.01 eV/Å.

In most of the computational tests, we have evaluated an average redox voltage using Eq. (1), where concentrations $x_1$ and $x_2$ correspond to fully intercalated and deintercalated cases (100% and 0%, respectively). The two exceptions are NaMnO$_2$ and NaCuO$_2$ layered structures, where we have evaluated a large number of possible models of partially deintercalated structures (Na$_{x_0/2}$MnO$_2$ and Na$_{x_1/2}$CuO$_2$) to calculate the voltage in the respective Na concentration ranges.
IV. EVALUATION OF REDOX VOLTAGES OF CATHODE MATERIALS

A. Materials with large charges in both spin channels of $d$-states, localized on TM cations: LiNiO$_2$, K$_2$(VOHPO$_4$)$_2$(C$_2$O$_4$)$_3$, and Na$_3$Ni$_5$(PO$_4$)$_3$P$_2$O$_7$

The redox potentials (calculated and experimental) and the values of $R$ parameter for materials of group (1) are provided in Table I (the values of $U$ and $U^{1/2}$ parameters for all studied materials are given in Appendix B). Table I clearly shows that $R$ parameters of three structures of this group are quite large (above 0.8). As we have discussed above, the standard DFT+$U$ approach, parameterized by LR, provides a substantially underestimated redox voltage as compared to experiment (e.g., 3.31 V vs 3.85 V for LiNiO$_2$). However, we find that the calculated redox voltages are in closer agreement with the experiment when the extended functional is employed (Table I).

In this work, we adopted ferromagnetic ordering of Ni cations for both intercalated and deintercalated forms of LiNiO$_2$. For the fully intercalated case, we used O3 type of structure, as denoted by the Delmas notations. For the desodiated NiO$_2$ configuration, we have tested the stability of O3 and O1 structures. When DFT+$U$/LR calculations are applied, we find that the O1 configuration is more stable. Therefore, the O1 structure has been used for the evaluation of the redox voltage using Eq. (1). However, when the extended functional is applied, we find that the O3 structure is more energetically favorable than O1 for NiO$_2$. Therefore, the O3 structure has been used for NiO$_2$ when the redox voltage has been evaluated using the extended functional (in case if a less stable O1 structure is employed, the voltage of 3.79 V has been predicted using the extended functional).

Another example of a material where the standard DFT+$U$/LR approach predicts a very underestimated potential is the K$_2$(VOHPO$_4$)$_2$(C$_2$O$_4$)$_3$ structure. This structure is very suitable for our test, as the voltage profile is largely a flat plateau with a characteristic value of 4.3 V (we perform a comparison with the measurements of the first charging experimental curve). Similar to LiNiO$_2$, our DFT+$U$/LR calculations provide an underestimated redox voltage of 3.54 V (Table I). The underlying reason for this poor computational ability is also very similar to LiNiO$_2$: the charges in majority and minority channels of K$_2$(VOHPO$_4$)$_2$(C$_2$O$_4$)$_3$ are quite substantial, as attested by the large value of $R$. Applying the extended functional [Eq. (6)], where the values of $U^{1/2}$ have been evaluated using Eq. (7), we find a redox voltage of 4.06 V, in better agreement with the experiment.

TABLE I. Computed voltages $\Phi_r$ (given in V) and $R$ parameters for the group (1) materials. Linear response (LR) and extended functional (ext.) results are provided. Experimental average voltages (exper.) are presented for comparison.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Phi_r$ (LR)</th>
<th>$R$</th>
<th>$\Phi_r$ (ext.)</th>
<th>$\Phi_r$ (exper.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNiO$_2$</td>
<td>3.31</td>
<td>0.98</td>
<td>3.64</td>
<td>3.85</td>
</tr>
<tr>
<td>K$_2$(VOHPO$_4$)$_2$(C$_2$O$_4$)$_3$</td>
<td>3.54</td>
<td>0.81</td>
<td>4.06</td>
<td>4.30</td>
</tr>
<tr>
<td>Na$_3$Ni$_5$(PO$_4$)$_3$P$_2$O$_7$</td>
<td>4.07</td>
<td>0.9</td>
<td>4.55</td>
<td>4.80</td>
</tr>
</tbody>
</table>

We have also performed an analysis of the high voltage Na$_3$Ni$_5$(PO$_4$)$_3$P$_2$O$_7$ structure for which DFT+$U$/LR predicted the underestimated average potential (4.07 V vs 4.80 V in the experiment). As could be seen in Table I, a large value of $R$ indicates that inclusion of additional corrections provided in Eq. (6) is also necessary for this material.

Applying additional corrections [Eq. (6)], we find that the deintercalated structure [Na$_3$Ni$_5$(PO$_4$)$_3$P$_2$O$_7$] can adopt two possible magnetic configurations: one with zero and the other with non-zero magnetic moments of Ni cations. The structure with zero magnetic moments is found substantially higher in energy, and therefore, we used the energy of the structure with non-zero magnetic moments for the calculation of the average redox voltage in Eq. (1). Using the extended functional approach [Eq. (6)], our calculations predict a more accurate value of redox voltage equal to 4.55 V.

B. Materials with intermediate charges in spin channels of $d$-states, localized on TM cations (LiVPO$_4$F structures and LiFePO$_4$)

We start the analysis of the materials of group (2) from two types of cathode materials, with identical stoichiometry (LiVPO$_4$F), which, however, have different atomic structures and electrochemical properties. For brevity, we denote the structure with orthogonal lattice vectors as OLV’s and the structure with non-orthogonal lattice vectors as NLVs. The results of our calculations for the materials of group (2) are provided in Table II. As shown in Table II, smaller values of $R$ parameters correspond to the materials of this group as compared to those of group (1). This is corroborated by PDOs of $d$-states of TM cations, shown in Fig. 2 (left and middle). Nevertheless, the neglect of corrections of interactions between the electrons with opposite spins could be a possible reason for the much underestimated average potential for OLV predicted by the DFT+$U$/LR method (Table II).

Applying the extended functional with the $U^{1/2}$ parameter evaluated using Eq. (7), we obtain an average potential in much closer agreement with the experiment for OLV. We should note that underestimation of the average potential predicted by the DFT+$U$/LR approach (by 0.4 V) is lower for this material than for LiNiO$_2$ and K$_2$(VOHPO$_4$)$_2$(C$_2$O$_4$)$_3$ (by 0.54 V and 0.76 V, respectively). For this reason, smaller corrections are needed to recover a more accurate value, as provided by Eq. (7).

With regard to the NLV structure, we find that DFT+$U$/LR calculations provide an underestimated value of the redox potential of 4.08 V, which is only slightly lower than the experimental value of...
4.27 V. However, additional corrections using the extended functional provide an average potential of 4.42 eV, which is even closer to the experimentally measured one, although slightly overestimated.

It is of interest to compare our findings on the two discussed LiVPO₄F configurations and explain a higher redox voltage for the NLV structure. First, we find that U parameters determined for DFT+U+U₁₁ calculations adopt very similar values for intercalated and deintercalated cases (these are obtained via LR parameterization, see Table V of Appendix B). Moreover, U₁₁ parameters employed for calculations using the extended functional are also very similar for these two structures. Nevertheless, the intercalated NLV is found to be 0.56 eV lower in energy per LiVPO₄F formula unit compared to the intercalated OLV (when applying calculations with the extended functional). On the other hand, deintercalated structures have very similar energies with the OLV structure being only slightly more favorable (by 0.01 eV) for a single formula unit VPO₄F.

We assume that a possible reason of a higher stability of the NLV structure in intercalated form could be the presence of Li–F bonds in this configuration, in contrast to OLV, where all Li are bonded only to nearby oxygens and no bonds are formed with fluorine anions. On the other hand, much closer energies of the deintercalated structures of NLVs and OLVs could be caused by the absence of strong Li–F bonds in both configurations due to the removal of Li cations.

Another example of a material with intermediate charges in spin channels is LiFePO₄. In our previous work, we have calculated the redox voltage of this material, reporting a slightly overestimated value of 3.7 V as compared to the experimental value of 3.5 V. Additional corrections using the extended functional in Eq. (6) provide numerically the same voltage of 3.7 V. Thus, for LiFePO₄, whose R parameter is close in value to those of other two structures of group (2), the voltage calculated using the extended functional is almost identical to that predicted using the DFT+U/LR method.

We should also note that a somewhat overestimated voltage computed for LiFePO₄ could be caused by the overestimated theoretical value of magnetic moments of Fe cations. For instance, for Fe sulfates, which have a similar electronic structure to Fe phosphate, we employed the same extended functional for bringing redox and magnetic properties to better agreement with experiment. However, the choice of the U₁₁ parameter is based on a different reasoning for these sulfate materials [as compared to Eq. (7)]. A possible reason for the poor performance of DFT+U/LR in this case could be related to incorrect alignment of PDOSs of majority and minority channels according to DFT calculations. Further analysis of such structures should be done in future studies.

C. Material with low charges in one of the spin channels of d-states, localized on TM cations: NaMnO₂

The voltage profile of NaMnO₂ has been measured in the work of Ma et al. The voltage is nearly constant at high concentrations of Na (from 100% to 60% approximately) with the respective value of about 2.65 V. A steady voltage increase has been observed upon further Na removal. In another study conducted by Li et al., the structure with Na₅/₈MnO₂ stoichiometry has been identified experimentally and theoretically as a distinctive configuration with a low energy.

Recently, we performed a detailed analysis of a voltage profile of NaMnO₂ using DFT+U/LR calculations. Our study has shown that a configuration with Na₅/₈MnO₂ stoichiometry, structurally very similar to the one, analyzed by Li et al. (these two are nearly degenerate in energy) indeed possesses an exceptional stability. DFT+U/LR calculations demonstrated nearly a constant voltage for high Na concentrations (100%–62.5%) and steady voltage increase for low Na concentrations (62.5%–0%) upon Na removal.

In order to test the performance of the extended functional in Eq. (6), we choose to calculate the voltage in the range of 100%–62.5% Na concentrations, adopting our structure with 62.5% Na concentration (V₁₁). Additionally, we also calculated an average voltage for the change of Na concentration from 62.5% to 0% (complete deintercalation), assuming that the voltage change is close to linear in this range (V₂). Thus, for NaMnO₂, we provide two values of the calculated redox voltages: V₁₁ and V₂.

Our calculations using the DFT+U/LR approach predict the values of V₁₁ and V₂ to be in good agreement with experiment (see Table III). As could be seen from PDOSs of d-states localized on Mn cations, the charges in one of the spin channels are significantly lower than the charges in the other channel (Fig. 2). For this reason, the value of parameter R provided by Eq. (7) is also small for this material. Such a small value of R leads to a small increase in the calculated redox voltages V₁₁ and V₂ when the extended functional given in Eq. (6) is applied. Therefore, calculations with the extended functional are also in a reasonable agreement with the experimental values and DFT+U/LR calculations.

D. Special cases: LiCoO₂, LiTIS₂, and NaCuO₂

In this subsection, we analyze materials for which the standard DFT+U/LR method provides reasonable values of the average redox potential, although d-states of these structures are featured by substantial charges in both majority and minority spin channels (see Table IV for collection of results). Similar to our previous study on LiCoO₂, we find that the DFT+U/LR approach provides a very reasonable redox potential of 4.06 V, in good agreement with the experimental value of 4.1 V. In our previous work, we performed calculations for the deintercalated structure with O₁ symmetry. Therefore, herein, we also adopted the O₁–CoO₂ structure for the analysis of the redox potential of LiCoO₂.

It is obvious from the value of the R parameter for LiCoO₂/CoO₂ couple that additional corrections should be applied for interactions between the electrons with opposite spins in view of strong Li–F bonds in both configurations due to the removal of Li cations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Φᵣ (LR)</th>
<th>R</th>
<th>Φᵣ (ext.)</th>
<th>Φₑ (exper.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaMnO₂ (low)</td>
<td>2.76</td>
<td>0.27</td>
<td>2.77</td>
<td>2.65</td>
</tr>
<tr>
<td>NaMnO₂ (high)</td>
<td>3.35</td>
<td>0.27</td>
<td>3.51</td>
<td>3.43</td>
</tr>
</tbody>
</table>

TABLE III. Computed voltages Φᵣ (given in V) and R parameters for the group (3) materials. Linear response (LR) and extended functional (ext.) results are provided. Experimental average voltages (exper.) are presented for comparison.
TABLE IV. Computed voltages $\Phi_i$ (given in V) and $R$ parameters for the group (4) materials. Linear response (LR) and extended functional (ext.) results are provided. Experimental average voltages (exper.) are presented for comparison. For LiCoO$_2$, we provide the value of $R$ calculated with $U_{1\uparrow}$ = 0 to demonstrate the presence of large charges in both spin channels (self-consistent evaluation of $R$ is not possible for CoO as mentioned in the text).

<table>
<thead>
<tr>
<th>Material</th>
<th>$\Phi_i$ (LR)</th>
<th>$R$</th>
<th>$\Phi_i$ (ext.)</th>
<th>$\Phi_i$ (exper.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>4.06</td>
<td>0.92</td>
<td>...</td>
<td>4.10$^{27}$</td>
</tr>
<tr>
<td>LiTiS$_2$</td>
<td>2.09</td>
<td>0.90</td>
<td>2.51</td>
<td>2.10$^{28}$</td>
</tr>
<tr>
<td>NaCuO$_2$</td>
<td>4.15</td>
<td>1.00</td>
<td>4.09</td>
<td>3.95$^{29}$</td>
</tr>
</tbody>
</table>

of substantial charges in both spin channels (Table IV). However, our attempts to apply these corrections, using the values of $U_{1\uparrow}$, according to Eq. (6) face technical difficulties. In particular, for the CoO$_2$ structure, convergence of calculations has not been achieved if $U_{1\uparrow}$ values are introduced. As a simple solution of this problem, we recommend employing a standard DFT+$U$/LR method for the evaluation of the redox voltage of LiCoO$_2$ in view of its higher computational stability and very reasonable value of the predicted redox potential.

The other cathode structure that, in principle, requires introduction of additional corrections using Eq. (6) is LiTiS$_2$, also due to the substantial value of $R$ (Table IV). Applying the DFT+$U$/LR method, we find a redox potential of 2.09 V, in very good agreement with the experimental value of 2.1 V.$^{28}$ This material is a conductor, which, as we noted in our previous report, could explain a very reasonable redox voltage of 1.88 V, predicted when a pure DFT is employed (setting $U = 0$).$^{26}$ Applying the extended functional according to Eq. (6), an overestimated voltage of 2.51 V is predicted. A possible reason for this inaccurate prediction for LiTiS$_2$ could be unphysical localization of $d$-states of Ti cations caused by Hubbard corrections in Eq. (6) for this conducting material.

To further corroborate the high degree of delocalization of $d$-states on Ti cations, we have evaluated the ratio $\text{Tr}[n_{\uparrow}n_{\downarrow}]/\text{Tr}[n_{\uparrow}]$ for both spin channels $\sigma$. The values of this ratio are 0.57 and 0.20 for majority and minority spins, respectively, indicating a large degree of delocalization due to considerable deviation from 1. For this reason, application of corrections assuming a full localization limit [Eq. (6)] is not fully justifiable, leading to the overestimated voltage for LiTiS$_2$. In comparison, much larger values of $\text{Tr}[n_{\uparrow}n_{\downarrow}]/\text{Tr}[n_{\uparrow}]$ for LiNiO$_2$ (0.95 and 0.87 respectively) show suitability of the employed corrections [Eq. (6)] despite crossing of a Fermi level by PDOSs of the majority channel (Fig. 2, left). Due to these observations, similar to the case of LiCoO$_2$, we propose either applying a standard DFT+$U$/LR approach for the evaluation of redox properties of LiTiS$_2$ or even relying on a usual DFT method, setting the value of $U$ to zero.

We have also calculated the redox potential of the recently studied NaCuO$_2$ structure synthesized as a potential candidate for a cathode material.$^{30}$ We need to note that due a very large hysteresis and hence very low discharge voltages alongside with a capacity fade, a possible application of this material as a cathode of the Na-ion battery could be problematic. However, we find this compound very attractive for testing purposes as it allows us to test the accuracy of the extended functional for another structure, with substantial charges in majority and minority channels and with Cu as a TM cation. Moreover, the charge curve of NaCuO$_2$ is nearly a flat plateau up until a removal of about a half of Na, allowing for a relatively simple estimation of voltage in this concentration range using Eq. (1).

For the calculation of redox voltage in this range, we have studied a large number of possible structures with 50% of Na concentration (150 models) selecting the most stable configuration. Subsequently, we applied DFT+$U$/LR and then the extended functional for the evaluation of the redox voltage. Calculations revealed that both approaches predicted an experimental redox potential of about 4 V with a very good accuracy: 4.15 V using the DFT+$U$/LR method and 4.09 V using the extended functional. This result is somewhat peculiar as the values of $U_{1\uparrow}$ parameters are quite large for this material (−4.26 and −4.57 eV for NaCuO$_2$ and Na$_{1/2}$Cu$_2$O$_2$, respectively, Table V of the Appendix B).

We wish to discuss further this unusually small impact of $U_{1\uparrow}$ on the evaluated redox voltage using Eq. (1). In addition to the described analysis, we have also applied a standard approach for the evaluation of redox voltage employing the same value of $U$ parameter for the evaluation of total energies of NaCuO$_2$ and Na$_{1/2}$Cu$_2$O$_2$ structures.$^{31}$ A wide range of $U$, from 0 to 9 eV has been investigated. We find that the redox voltage depends very weakly on the $U$ parameter: it changes from 3.60 to 3.95 V upon increase in $U$ from 0 to 9 eV.

Moreover, given identical PDOS of $d$-states of two spin channels localized on Cu cations for NaCuO$_2$ and for Na$_{1/2}$Cu$_2$O$_2$ structures, we need to point out that extended functional [Eq. (6)] is identical to the more common form in Eq. (3), albeit with double values of $U$ parameter in Eq. (3). Although in the case of other materials (e.g., LiNiO$_2$), this increase in $U$ resulted in a larger value of voltage, a very weak dependence of voltage from the values of $U$ parameters (keeping a similar difference for NaCuO$_2$ and Na$_{1/2}$Cu$_2$O$_2$) explains that both DFT+$U$/LR and extended functional give very similar results for NaCuO$_2$.  

V. SUMMARY AND CONCLUSIONS

In this work, we have shown that extension of the DFT+$U$/LR method could be necessary, particularly for the evaluation of redox voltages of cathode materials with substantial electronic charges present in both spin channels of $d$-states, localized on TM cations. This lack of accuracy of the DFT+$U$/LR method is not unexpected and stems from uncorrected interactions between electrons with opposite spins. As a remedy, we propose employing an extended DFT+$U$+$U_{1\uparrow}$ functional, which provides additional corrections for this type of interactions [Eqs. (6) and (7)].

We classified the studied materials into three groups depending on the strength of interactions between the electrons with opposite spins. In addition, we also introduced a special fourth group of materials, well described by the DFT+$U$/LR method, despite large charges present in both spin channels of the respective TM cations. The calculated voltages for all studied groups of materials [using DFT+$U$/LR and extended functional, Eq. (6)] are presented in Fig. 3 alongside with the experimental findings (for convenience, we
highlighted each group by the distinctive color in Fig. 3). We also provided the ranges of parameter $R$ [expression is given in Eq. (7)], which is used for the evaluation of the $U_{\uparrow \downarrow}$ parameter and characterizes the magnitude of additional corrections of interactions between the electrons with opposite spins.

As shown in Fig. 3, the structures of group (1) (the left side, blue area) are featured by the very underestimated redox voltages when the DFT+$U$/LR method is applied. However, larger values are obtained when using the extended DFT+$U+U_{\uparrow \downarrow}$ method, resulting in better agreement with experiment. Similarly, for the group (2) (green area in Fig. 3), clear improvement could be observed when additional corrections are applied. However, Fig. 3 also demonstrates that DFT+$U$/LR calculations provide better agreement between the calculated and experimental redox voltages for materials of group (2) as compared to the materials of group (1). In addition, the values of $R$ parameters are smaller for group (2), resulting in a smaller change in redox voltages predicted by DFT+$U$/LR.

For group (3) (red area in Fig. 3), we find that additional corrections are not necessary as the DFT+$U$/LR method provides accurate values of redox voltages. Nevertheless, predictions using the extended functional are also reasonable, in good agreement with DFT+$U$/LR results. It is clear that small charges in one of the spin channels make interactions between the electrons with opposite spins significantly weaker, resulting in much smaller additional corrections.

The special category of materials belong to the group (4), where DFT+$U$/LR calculations provide reasonable redox voltages despite large charges in both spin channels of respective TM (hence large values of $R$). For group (4) (gray area in Fig. 3), we find that LiTiS$_2$ is best described by the DFT+$U$/LR method, whereas the extended functional provides an underestimated voltage, possibly due to the metallic electronic structure of this material. For LiCoO$_2$, we provide the results of the DFT+$U$/LR method exclusively due to technical problems of convergence when additional corrections are applied. For NaCuO$_2$, we find that both methods provide very similar predictions in good agreement with the experiment. Based on these results, we recommend applying a standard DFT+$U$/LR method for materials of group (4) and possibly also for other structures, which contain respective TM cations.

Before ending this work, we wish to comment on how the other elements of cathode structures, namely, alkali metals and anions, affect the accuracy of prediction of redox voltages using discussed DFT+$U$/LR and extended methods. First, the type of alkali metal cation (Li, Na, K) does not seem to be a critical factor, which influences the accuracy of the voltage calculation. As a word of caution, we need to state that more tests are needed to further corroborate this conclusion. Second, we also analyzed materials with various types of anions, such as oxide materials with oxygen as an anion, one sulfide material, phosphate materials with PO$_4$ polyanion, structures with F anions, and even organic structure with negatively charged oxylate [(C$_2$O$_4$)$_2]^{2-}$ as well as PO$_4$ and OH anions.

We find that despite a rich diversity of types of anions in the studied materials, the accuracy of our calculations seems to be independent of the anion type. For instance, very good agreement with experiment is demonstrated for LiVPO$_4$F, whereas less accurate results are obtained for LiNiO$_2$, which contains a more simple oxygen anion. Nevertheless, the role of anions could be critical, as for Fe-based sulfates, where the DFT+$U$/LR method was found less accurate than for LiFePO$_4$, although it is possible that interactions between the $d$-states with opposite spins are a more decisive factor responsible for the poor accuracy of the predicted voltages for Fe-based sulfates (see Ref. 19 for further details). Overall, the key finding of our work is that interactions between the $d$-states do require careful corrections, including those with the same spin as well as the states with opposite spins.

ACKNOWLEDGMENTS

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APPENDIX A: COMPARISON OF COMPUTATIONAL METHODS

Three types of interactions, namely, Coulomb interactions between the electrons with the same spins, exchange interactions
(also between the electrons with the same spins), and Coulomb interactions between the electrons with opposite spins, can be parameterized by \( U, J \), and \( U_1 \) parameters, respectively. As we have already pointed out in Ref. 19, the impact of the \( U \) parameter in Dudarev’s and Liechtenstein’s methods on Coulomb interactions between the electrons with the same spins has very similar effect (see Appendix B of Ref. 19). Herein, we also discuss the impact of the \( J \) parameter present in both methods on the exchange interactions.

In Fig. 4, we demonstrate the impact of \( J \) on the total energy of LiNiO\(_2\) used here for testing purposes (when \( J = 0 \), both energies are nearly identical). Calculations show that higher values of \( J \) lead to the energy decrease for LiNiO\(_2\). However, this change is greater in the method of Liechtenstein et al. The different impact of \( J \) is not surprising as exchange interactions are described using different expressions in these two methods.

Comparison of the performance of the method of Liechtenstein et al. and Eq. (6) is more complicated. The main reason here is the difficulty to evaluate the \( J \) parameter computationally. Although expressions for \( U \) and \( J \) have been provided previously in the literature, these are only valid if interactions between the electrons with opposite spins are described by the same \( U \) parameter. However, as we pointed out previously, the respective Hubbard term is fully removed by dcc for these interactions.\(^{19}\) For this reason, \( J \) could not be calculated as a derivative of energy over magnetization. In passing, we believe that modified corrections for electrons with opposite spins should be applied to the method of Liechtenstein et al. as well, which, however, could be addressed in future works.

We attempted to calculate redox voltages for several materials employing the method of Liechtenstein et al. via setting the same value of \( J \) for intercalated and deintercalated structures (\( U \) are evaluated using the LR method), as shown in Fig. 5. For this purpose, we have chosen materials, where the DFT+U/LR method provides the most inaccurate results (materials of group 1, Subsection IV A).

Our calculations show that setting finite values of \( J \) still keeps the calculated redox potentials very low (Fig. 5). In fact, even if a very large value of \( J = 3\) eV is adopted (\( J \) normally does not exceed 1 eV significantly), the calculated redox voltages are still much smaller than the experimental ones. For this reason, it seems that adjustment of \( J \) parameters in the method of Liechtenstein et al. is not an attractive route to obtaining accurate values of redox voltages. On the other hand, the calculations using Eq. (6) could provide better agreement with the experimental voltages, as shown in Fig. 3 (such calculations could also be parameterized computationally, as discussed in Sec. II B).

**APPENDIX B: EMPLOYED U AND U\(_1\) PARAMETERS**

The full list of \( U \) and \( U_1 \) parameters for all studied materials is provided in Table V.

**TABLE V.** The values of \( U \) and \( U_1 \) parameters for studied cathode materials (intercalated/deintercalated) given in eV. We provide our evaluated \( U \) using DFT+U/LR (U/LR) and extended functional \( U\text{(ext.)} \). For LiCoO\(_2\), we present the value of \( U \) determined within DFT+U/LR calculations exclusively (see the text for details).

<table>
<thead>
<tr>
<th>Material</th>
<th>( U ) (LR)</th>
<th>( U ) (ext.)</th>
<th>( U_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNiO(_2)</td>
<td>4.52/4.01</td>
<td>3.93/3.18</td>
<td>−3.80/−3.12</td>
</tr>
<tr>
<td>( K_2(VOHPO_4)_{2}(C_2O_4) )</td>
<td>2.68/2.50</td>
<td>2.53/2.39</td>
<td>−2.04/−1.93</td>
</tr>
<tr>
<td>( Na_4Ni_3(PO_4)_2P_2O_7 )</td>
<td>2.77/4.30</td>
<td>2.67/3.39</td>
<td>−2.41/−3.06</td>
</tr>
<tr>
<td>LiVPO(_4)(_F) (NLV)</td>
<td>2.71/3.0</td>
<td>2.69/2.97</td>
<td>−1.04/−1.15</td>
</tr>
<tr>
<td>LiVPO(_4)(_F) (OLV)</td>
<td>2.63/3.0</td>
<td>2.68/2.93</td>
<td>−1.08/−1.19</td>
</tr>
<tr>
<td>LiFePO(_4)</td>
<td>2.30/3.75</td>
<td>2.35/3.73</td>
<td>−0.92/−1.46</td>
</tr>
<tr>
<td>NaMnO(_2) (low)</td>
<td>3.63/3.83</td>
<td>3.71/3.80</td>
<td>−1.02/−1.04</td>
</tr>
<tr>
<td>NaMnO(_2) (high)</td>
<td>3.83/4.06</td>
<td>3.80/4.04</td>
<td>−1.04/−1.11</td>
</tr>
<tr>
<td>LiCoO(_2)</td>
<td>3.60/3.94</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>LiTiS(_2)</td>
<td>3.43/3.48</td>
<td>3.36/3.25</td>
<td>−2.38/−2.30</td>
</tr>
<tr>
<td>NaCuO(_2)</td>
<td>5.52/5.97</td>
<td>4.26/4.57</td>
<td>−4.26/−4.57</td>
</tr>
</tbody>
</table>
DATA AVAILABILITY

The data that support the findings of this study are available within the article.

REFERENCES