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研究成果の概要(和文)：反平行スピンを持つ電子間相互作用の補正に基づく新規なDFT+U汎関数を設計する。提案された汎関数のパラメータ化を行い NaMnO₂カソードの電圧プロファイルの評価へ応用する(関連するパラメータの計算による評価)。また提案された汎関数についてベンチマーク計算を行う(酸化物、リン酸塩、構造を含む10種類のカソード材料のテスト)。

研究成果の学術的意義や社会的意義

A novel method that could be used for accurate evaluation of voltages of cathode materials of Li- and Na-ion batteries has been proposed and tested.

研究成果の概要(英文)：Design of the novel DFT+U functional, that introduces corrections of interactions between the electrons with opposite spins. Parameterisation of the proposed functional (computational evaluation of involved parameters). Application to evaluation of a voltage profile of NaMnO₂ cathode. Benchmarking of the proposed functional (testing on 10 cathode materials, including oxides and phosphates).

研究分野：electrochemistry

キーワード：DFT+U battery cathode

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1. 研究開始当初の背景

Computational evaluation of chemical properties of transition metal compounds is a challenging task due to difficulties of attaining a high accuracy of calculated quantities as compared to experiments, as well as other issues such as high computational cost or reliance on fitting procedures. DFT+ U method is a very instrumental tool, which is widely used in analysis of transition metal oxides as a reasonable compromise between accuracy and computational cost. For instance, this method has been successfully applied for reliable predictions of redox voltages of cathode materials of Li- and/or Na-ion batteries, where a large amount of calculations might be necessary (e.g. when entire voltage profiles are calculated, etc.).

One of the key limitations of DFT+ U method is a general reliance on empirical search for an employed value of U parameter. Although acceptable in many studies, empirical approach might be problematic to apply when experimental data is not available, which is often the case for recently employed or even not yet synthesized materials. Moreover, ever-growing complexity of cathode structures pose even greater challenge due to borrowing of U values obtained via benchmarking of more simple materials. As a result, additional readjustment of U values for materials of higher complexity has been reported.

As alternative to empirical fitting, U parameters could be evaluated computationally. For instance, linear response method has been applied for analysis of redox voltages of cathode materials. More recently the applicant implemented and applied self-consistent evaluation of U values into the VASP code, generally providing redox voltages in a good agreement with experimental measurements (Fig. 1) [1]. However, subsequent study has shown that entire class of important Fe-based sulfate structures could not be accurately described by this method, yielding very overestimated values for redox voltages and too high values for magnetic moments as compared to experiment [2]. A possible solution was proposed by the applicant in a form of additional contributions to Hubbard term, which account for corrections due to interactions between the electrons with opposite spins [2].

2. 研究の目的

Although an improved agreement with experiment has been achieved using extended DFT+ U method [2], several methodological problems still required solution. First, the additional Hubbard term was not corrected (for double counting) as a DFT functional, causing problems in important tasks such as evaluation of atomic forces, etc. Secondly, parameterization of an additional term has been performed using empirical fitting, but not computational evaluation (as in the case of a standard DFT+ U). Additionally, more complex tests such as calculation of an entire voltage profile, rather than more simple calculation of average redox potentials needed to be performed. These aspects should be addressed for testing and further development of the proposed methods.

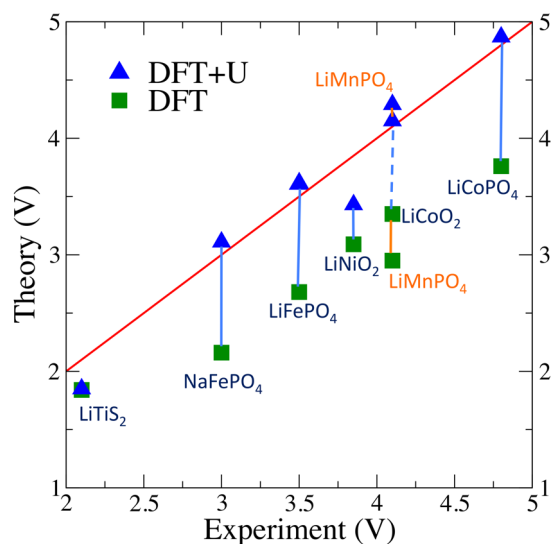


Figure 1 Redox potentials calculated by DFT and DFT+ U methods.

In view of the discussed shortcomings of the proposed extended DFT+ U method, this project aimed at:

- Introduction of double counting corrections to additional term of the extended DFT+ U functional. Important aspect in this regard has been formulation of Hamiltonian of an extended DFT+ U functional with proper treatment of double counting corrections;
- Deriving and implementing an expression for atomic forces due to extended functional;
- Adjustment of band gaps when necessary;
- Search for computational procedure, that allows for evaluation of a parameter due to an additional term in the extended DFT+ U functional (validity was tested on 10 cathode materials, Fig. 2);
- Testing of computationally parameterized DFT+ U method for prediction of voltage profile of a cathode material (as opposed to a simpler evaluation of an average redox potential).

3. 研究の方法

This work employed DFT+ U framework, as implemented into VASP code as a starting point. Linear response parameterization has been introduced [1]. This implementation differs from previous works by self-consistency of calculation of a U parameter, evaluating a response of DFT+ U charge density (in contrast to DFT charge density as in previous works).

Extended DFT+ U method (subsequently titled as DFT+ $U+U_{\uparrow\downarrow}$) has been derived and implemented with proper treatment of double counting corrections due to additional term [3]. For correction of too narrow band gaps, the scissor operator has been implemented (expressions for PAW formalism, which are subject to generalized orthogonality conditions in contrast to more common orthogonality of electronic bands have been derived) [3]. A procedure for computational evaluation of an additional $U_{\uparrow\downarrow}$ parameter has been developed and implemented [4].

4. 研究成果

Calculations using proposed extended DFT+ U method have been applied for evaluation of redox potentials of Fe-based sulfates, which could find application as cathode materials for Li- and Na-ion batteries due to high operating potential [3]. In contrast to standard DFT+ U approach, extended functional calculations provided improved agreement for redox voltage for Fe-based sulfates. Moreover, better agreement has been achieved for a magnetic moment of Fe cation (as compared to reported experimental value for $\text{Li}_2\text{Fe}(\text{SO}_4)_2$). Additionally, formation energies of Fe oxides (Fe_2O_3 and Fe_3O_4) were also found to be in a better agreement with experiment. Similarly, magnetic moments of Fe have been also adjusted to better agreement (as compared to standard DFT+ U calculations).

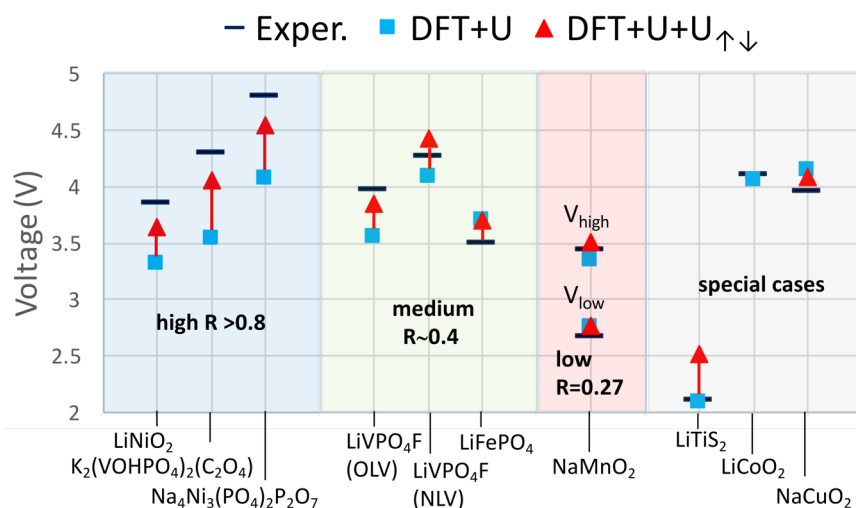


Figure 2 Redox voltages calculated by extended and standard DFT+ U .

As the next step, the method that allows for full parameterization of DFT+ $U+U_{\uparrow\downarrow}$ approach has been proposed and tested (Fig. 2) [4]. Both involved parameters (U and $U_{\uparrow\downarrow}$) have been calculated using linear response approach. An expression for an additional parameter ($U_{\uparrow\downarrow}$)

has been derived, based on the ratio of localized electronic charges in two spin channels [4]. Much improved agreement with experiment has been achieved for materials where standard DFT+ U method provide very underestimated voltages (e.g. LiNiO₂ in Fig. 2). A poor agreement, obtained by DFT+ U method has been explained by the absence of corrections for interactions between the electrons with opposite spins [4]. Such corrections are however present in the extended functional, resulting in a better agreement with experiment (Fig. 2). On the other hand, for materials, where the ratio of spin up and spin down charges is lower, both DFT+ U functionals provided accurate values. This is not surprising as for such cases additional term gains smaller values. Overall, this study has shown that extended functional could provide accurate predictions of redox voltages for a wide range of cathode structures, which include various types of transition metals.

DFT+ U , parameterized by linear response evaluation of U parameters has been also applied for calculation of a voltage profile of NaMnO₂ material (Fig. 3) [5]. The challenge in such application is associated with the need for determination of structures of partially desordiated material (ground states for respective concentrations) and calculation of respective redox voltages. As is shown in Fig. 3 thus calculated voltage profile is in better agreement with experimental measurements as compared to calculations with a fixed value of a U parameter (upper panel) or results from the literature where constant value of U has been used (medium panel). Additionally, parameterized DFT+ U calculations correctly predicted exceptional stability of Na_{5/8}MnO₂ structure in agreement with earlier experimental identification. Indeed, a respective step is present in computed voltage profile at respective Na concentration (62.5%). In contrast, calculations with a fixed value of U parameter do not predict a step at this concentration (Fig. 3) and therefore can not account for a high stability of Na_{5/8}MnO₂ structure observed experimentally.

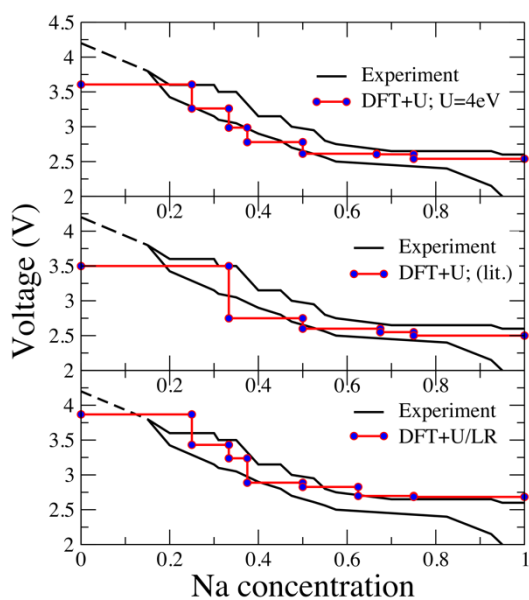


Figure 3 Voltage profile. Linear response calculations are at the bottom panel.

Overall, a new extended DFT+ $U+U_{\uparrow\downarrow}$ functional has been formulated and implemented within this work. Tests have shown a further improvement of computed properties (such as redox potentials and magnetic moments) as compared to a standard DFT+ U . Additionally, it has been demonstrated that even entire voltage profile could be calculated in a good agreement with experiment, fully avoiding experimental fitting.

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5. 主な発表論文等

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3. 雑誌名 The Journal of Physical Chemistry C	6. 最初と最後の頁 1531 ~ 1543
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1. 著者名 Maxim Shishkin* and Hirofumi Sato	4. 巻 main author
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掲載論文のDOI (デジタルオブジェクト識別子) 10.1063/5.0039594	査読の有無 有
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掲載論文のDOI (デジタルオブジェクト識別子) 10.1063/1.5090445	査読の有無 有
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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

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