Comparative study on the electronic structures and redox reactions in LiCrX₂ and NaCrX₂ (X = O and S)

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LiCrO₂ and NaCrO₂ have been well-studied as cathode materials in lithium and sodium ion batteries, while the studies on LiCrS₂ and NaCrS₂ are relatively rare. In this work, a comparative study on the electronic structures and redox reactions in oxides (LiCrO₂, NaCrO₂) and sulfides (LiCrS₂, NaCrS₂) is performed. A first-principles method has been used to calculate the Bader charge transfer, the electronic structures and the magnetic moments during the entire delithiation or desodiation process. The Bader charge analysis suggests that all the S, O and Cr ions in LiCrX₂ and NaCrX₂ participate in the redox reactions, where the loss of electrons of S ions is clearly larger than that of O ions. Besides, the redox processes of Cr ions are of much less significance. It is noted that, in the sulfides, Cr ions even gain a small portion of electrons rather than losing electrons during the extraction of Li/Na ions. All the charge transfer happens between the S-3p/O-2p and the Cr-3d bands. The redox reactions of O or S ions originate from the energy levels of O/S being pushed towards/across the Fermi surface due to the strong p–d hybridization.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable energy storage devices and consumer electronics, such as cell-phones, laptops and even electric vehicles. Though LIBs have dominated the rechargeable battery market due to their excellent performances, lithium resources may not be sufficient to meet the increasing global demand for batteries. Compared with LIBs, sodium-ion batteries (SIBs) not only have similar electrochemical mechanisms, but there are also abundant sodium resources on the earth. No matter what type the battery is, capacity is one of the most important parameters. Over the past decades, a great deal of effort has been made to improve the capacity of cathode materials. The anionic redox may increase the capacity of cathode materials, therefore, extensive studies have been made on the anionic redox reactions from both the experimental and theoretical sides. Based on the first-principles calculations, Ceder et al. found that oxygen participated in the redox reactions when Li₀.₅CoO₂ was at a high potential. The change of the electronic structure of O in Li₀.₅CoO₂ was experimentally observed by O K-edge X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). Furthermore, Ceder and co-workers uncovered that the structural origin of the oxygen redox reaction came from Li–O–Li configurations for lithium excess materials or Li/M disordered oxides. Moreover, sulfur ions also participate in the redox reactions, which will be discussed in detail in this work. Nowadays, the redox reaction processes are considered as an important issue in further developing the high-capacity electrodes.

Generally speaking, redox centers were regarded as metals for most of the cathode materials. However, in the study of NaCrS₂ by Shadike et al., Cr was found not to participate in the redox reactions while only the S²⁻ underwent oxidation/reduction during the charging/discharging processes. This phenomenon provokes us to study the redox reaction processes between the LiCrX₂ and NaCrX₂ (X = O and S). LiCrO₂ was thought to possess poor electrochemical properties. However, by tailoring the size of LiCrO₂, the poor electrochemical performances in the LiCrO₂ can be dramatically enhanced. Compared with the unremarkable properties of layered LiCrO₂ in LIBs, layered NaCrO₂ is a promising cathode material in SIBs. NaCrO₂ is also considered to be a safe electrode material since it is stable staying with the electrolyte of NaPF₆, as compared with the delithiated Li₀.₅CoO₂. In a word, LiCrX₂ and NaCrX₂ (X = O and S) show different properties in LIBs and SIBs. Hence, there is of significance to have a comparative study of the different electrochemical properties in Li and Na cells for LiCrX₂ and NaCrX₂ (X = O and S).

In this study, we focus on the redox reactions in the layered LiCrX₂ and NaCrX₂ (X = O and S) during the delithiation and desodiation processes. Based on the first-principles calculations, the charge transfer and the Bader charges are analyzed in...
order to understand the redox reaction processes in both LiCrX$_2$ and NaCrX$_2$ (X = O and S). We discover that all the Cr, O and S ions engage in the redox reactions in the four materials studied, where the loss of electrons by S ions are maximal. It is also found that, in the sulfides, Cr ions even gain a small portion of electrons rather than losing electrons during the extraction of Li/Na ions. The redox reaction processes are understood by the electronic structures and magnetization calculations during the charging/discharging processes.

2. Computational method

First-principles calculations were performed by using the projector augmented wave (PAW) scheme within the density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP). Exchange correlation energies were treated with the generalized gradient approximation (GGA) in the form proposed by Perdew, Burke, and Ernzerhof (PBE). To take into account the strong correlation effect of the transition metal Cr, we considered a Hubbard-like correction (GGA+U), with an effective interaction parameter $U_{eff} = U - J$ employed in the calculations. In order to ensure the correctness of the $U$ value, we have calculated Bader charge differences between $x = 6$ and $x = 0$ states as a function of $U$ values ($U = 1, 2, 3, 3.5, 4, 5$). From the calculation results in Table 1, we found that Bader charge differences for different $U$ values fluctuate inconspicuously. We therefore employ the $U$ value of 3.5 eV.

The wavefunctions of the system were expanded by plane waves, and the cutoff of the plane wave kinetic energies for the LiCrO$_2$/NaCrO$_2$ and LiCrS$_2$/NaCrS$_2$ systems were 600 eV and 500 eV, respectively. Brillouin-zone integrations were approximated by using special $k$-point sampling of the Monkhorst-Pack scheme with a $12 \times 12 \times 2$ grid for the primitive unit cell and a $6 \times 6 \times 2$ grid for the $2 \times 2 \times 1$ supercell.

The lattice constants and the atomic positions were fully relaxed before the calculations of the electronic structures. The convergence thresholds for optimization were set to $10^{-5}$ eV per atom in energy and 0.01 eV Å$^{-1}$ in force. Since the magnetic properties of Cr atoms might have important influences on the properties of the electronic structures of the materials, spin-polarized calculations were performed for all the systems. Moreover, a detailed exploration about charge transfer between atoms was made by the Bader charge analysis. The calculation of the redox reaction processes of the layered LiCrX$_2$ and NaCrX$_2$ (X = O and S) were carried out by a $2 \times 2 \times 1$ supercell, which contained 12 formula units. It was then possible for us to deintercalate 1 to 12 lithium or sodium ions in the supercell. In this study, we chose to deintercalate 1, 3, 4, 6, 8, 11, and 12 lithium or sodium ions, respectively, to investigate the redox reaction processes in the four materials.

3. Results and discussion

3.1 Electronic structures of LiCrX$_2$ and NaCrX$_2$ (X = O and S)

Table 2 shows the structural parameters and the corresponding experimental values of the relaxed LiCrX$_2$ and NaCrX$_2$ (X = O and S). LiCrO$_2$, NaCrO$_2$ and NaCrS$_2$ belong to $R3m$ space group with layered rock-salt structure ($\alpha$-NaFeO$_2$), as shown in Fig. 1a, c and d. However, the space group of LiCrS$_2$ is $P3m1$, as shown in Fig. 1b. For LiCrO$_2$, Li occupies 3a position, Cr occupies 3b position and O occupies 6c position, if represented by Wyckoiff position. For NaCrO$_2$ and NaCrS$_2$, the 6c position is again occupied by O or S atoms, while the 3a and 3b positions are occupied by Cr and Na, respectively (here, the atomic occupation is opposite to those in LiCrO$_2$). Besides, for LiCrS$_2$, Li occupies 1b position, Cr occupies 1a position and S occupies 6i position.

### Table 1

| $U$ value | 1  | 2  | 3  | 3.5 | 4  | 5  |
|-----------|----|----|----|-----|----|----|
| $\Delta Q$(Cr) | -0.10 | -0.07 | -0.09 | -0.12 | -0.07 | -0.09 |
| $\Delta Q$(O) | -0.17 | -0.18 | -0.18 | -0.16 | -0.19 | -0.20 |
All the four systems studied, i.e., LiCrX₂ and NaCrX₂ (X = O and S), are layered materials. These layered structures are composed of sheets of edge-sharing MO₆ octahedra (M = Li, Na, Cr), with M atoms occupy the center of the octahedra. The diversity of the layered materials is reflected by different orientations of sheets of edge-sharing MO₆ octahedra stacked along the c-axis direction. According to Delmas et al., the layered oxide with general formula AₓMO₃ can be classified into three groups, i.e., O type (octahedral), T type (tetrahedral) and P type (prismatic). The classification is based on the coordination polyhedron formed by A ions. As shown in Fig. 1, the coordination polyhedra formed by the alkali metal ions in the materials are all octahedrons. Except that LiCrS₂ is O₂ type, all the other three structures are O₃ type, here the number 2 or 3 represents the packing number of layers of the least repeating unit of oxygen or sulfur atoms in the unit cell. In the O type material, lithium/sodium ions should pass through the tetrahedra between octahedra during their diffusion, while in the P type material, lithium or sodium ions can directly diffuse between prisms, so that ions migration rate of P type material is usually higher than that of O type material.

In order to understand the electronic properties of LiCrX₂ and NaCrX₂ (X = O and S), we have calculated the spin-polarized band structures of these materials. It is shown that the electronic structures of NaCrX₂ are similar to those of LiCrX₂, so we will not go into the details of NaCrX₂ hereinafter. It can be seen from Fig. 2 that LiCrO₂ is an indirect bandgap semiconductor, with the conduction band minimum (CBM) of the spin-up band very much close to the M point, and the valence band maximum (VBM) near the L point along the A-L direction. The bandgap of the spin-up dispersion is 2.90 eV. On the other hand, the CBM of the spin-down band is located at the Γ point, the VBM is near the middle of the K and Γ points, and the bandgap of the spin-down bands is 4.25 eV. According to our calculation results, LiCrS₂ is also an indirect bandgap semiconductor. The spin-up bandgap is 1.16 eV. On the other hand, the spin-down bandgap is 2.18 eV. The bandgaps of LiCrS₂ are much smaller than those of LiCrO₂, since the electronegativity of S is smaller than that of O. From Fig. 2, the spin-up bands exhibit significant differences from the spin-down ones, indicating that LiCrO₂ is magnetic semiconductor with obvious spin polarization. Obviously, the electronic conductivity of these materials should be small when lithium or sodium ions are not extracted, due to the relatively large values of bandgaps. The conductivity of the materials could be improved by lithium/sodium deintercalations, carbon coating and doping.

For further understanding the bonding properties of the materials, we have calculated the deformation charge densities, shown by contour plots on two characteristic planes. Here, the deformation charge density is defined as the difference between the self-consistent charge density of the system and the superposition of the individual atomic charge densities, i.e.,

$$\Delta \rho(\vec{r}) = \rho(\vec{r}) - \sum_{\mu=1}^{N} \rho_{\text{atom}}(\vec{r} - \vec{R}_\mu)$$

where $\vec{R}_\mu$ are the atomic positions. Fig. 3a and b present the contour plots of the deformation charge density on (110) of the LiCrO₂ and LiCrS₂, respectively. It can be seen from Fig. 3a that charge accumulates around O, while charge reduces significantly around Cr, suggesting that Cr–O bonding is mainly ionic (also mixed with some covalent). However, in Fig. 3b, the plots indicate a strong covalent bonding between Cr and S atoms (also mixed with ionic character), compared with strong ionic character in Cr–O bond. In one word, comparing Fig. 3a with Fig. 3b, bonding characteristics between O–Cr–O are mainly ionic in LiCrO₂, while those between S–Cr–S are mainly covalent in LiCrS₂. We also discover that a significant number of electrons are transferred to O ions in LiCrO₂, compared with only a portion of electrons are moved to S ions in LiCrS₂. Such a feature is
consistent with the fact that the electronegativity of O is larger than that of S.

The population analysis is helpful for understanding the gain/loss of charges, where the detailed contributions from each atom and each atomic orbital to the electronic states (wavefunction) can be obtained. That is,

$$\psi_{nl}(\mathbf{r}) = \sum_{\mu=1}^{N} \sum_{\text{atomic}} C_{ln}(n, \tilde{\mathbf{r}}, \mathbf{R}_\mu) \psi_{\text{atomic}}^{nl}(\mathbf{r} - \mathbf{R}_\mu)$$

The coefficients $C_{ln}(n, \tilde{\mathbf{r}}, \mathbf{R}_\mu)$ could help analyze the hybridizations of atomic orbitals and the populations as well. Here, as an example, the electronic state (wavefunction) at the valence band maximum (VBM) is found to be contributed mainly by the $d_{x^2}$, $d_{xy}$, $d_{yz}$ states of Cr atoms.

### 3.2 The Bader charges and redox reaction processes

Upon charging, lithium or sodium ions deintercalate gradually from the cathode material under electric field. In order to calculate the Bader charges, the delithiation or desodiation processes should be determined. Here, we choose to deintercalate 1, 3, 4, 6, 8, 11 and 12 lithium or sodium ions in the supercell, respectively. Since there are numerous configurations have to be calculated during the charging processes, here, we describe an approximate scheme to obtain the minimum energy structure (MES) for Li$_{1-x/12}$CrX$_2$ and Na$_{1-x/12}$CrX$_2$ (X = O or S) at various lithium/sodium compositions. When only one lithium or sodium ion is to be deintercalated, we can easily consider all the non-equivalent lithium or sodium sites, since the number of equivalent sites is limited. When two lithium/sodium ions are deintercalated, the structures with nearest and farthest lithium/sodium ions are first calculated. Some other structures of the lithium/sodium ion pairs (not in the nearest or farthest) are carefully chosen, only these structures, but not all, are calculated to help judge the MES. When three lithium/sodium ions are to be extracted, all the possible structures where three lithium/sodium ions are in the nearest or farthest positions are first calculated. Some other structures of the lithium/sodium ion pairs (not in the nearest or farthest) are carefully chosen, only these structures, but not all, are calculated to help judge the MES. For more than three lithium or sodium ions are to be deintercalated, the same philosophy discussed above are applied. In fact, when $x = 12$, we have a definite structure to calculate, with all Li/Na ions extracted. When $x = 11$, the way for determining the lithium or sodium sites is equivalent to those of $x = 1$. Similarly, if $x = 10$, the situation is the same as $x = 2$, and so on.

To explore the redox reactions during the charging/discharging processes, we have calculated the Bader charges of the Li$_{1-x/12}$CrX$_2$ and Na$_{1-x/12}$CrX$_2$ (X = O or S, $x = 0, 1, 3, 4, 6, 8, 11, 12$). Fig. 4 shows the Bader charge loss/gain relative to the fully lithiated/sodiated phases ($x = 0$) for each $x$ composition, based on the first-principles calculations. As shown in Fig. 4, both the oxygen and sulfur ions lose electrons apparently (relative to O and S ions at $x = 0$) in either case, during the entire intercalation/deintercalation processes. However, it can be seen from Fig. 4 that Cr ions lose electrons in the oxides while gain electrons in the sulfides (relative to $x = 0$). It is noted that the gain/loss of charges of Cr ions are relatively less conspicuous as compared with those of O and S ions, among $x = 0$ to $x = 12$. For example, for the chromium in sulfides, Cr ions gain only a small number of electrons (less than 0.1 e) in the redox reactions. Moreover, the loss/gain of electrons by the Cr, O and S ions increase linearly as the extraction of lithium or sodium ions increase.

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**Fig. 4** The Bader charge per atom relative to the fully lithiated or sodiated phases ($x = 0$) for Cr, O and S ions in Li$_{1-x/12}$CrX$_2$ and Na$_{1-x/12}$CrX$_2$ (X = O or S), where the solid lines represent the Bader charges of LiCrX$_2$ and the dashed lines show the Bader charges of NaCrX$_2$ systems.

**Fig. 5** Sum of Bader charges per supercell for Li$_{1-x/12}$CrX$_2$ (X = O or S), where the solid and dashed lines represent the Bader charges of LiCrX$_2$ and NaCrX$_2$ systems, respectively. The dot-dashed line represents the correct number of electrons required to compensate for the charge loss during the delithiation or desodiation processes.
The sum of the Bader charges from Cr and O/S ions, relative to the fully lithiated/sodiated states, during the redox processes are shown in Fig. 5. Once a lithium or sodium ion is deintercalated, the remaining ions (i.e., Cr, O and S ions) have to compensate one electron. The dot-dashed line in Fig. 5 represents the number of electrons required to compensate for the charge loss due to delithiation/desodiation. The deviation from the dot-dashed line for the curves of the calculated Bader charges indicates the error of the Bader charge calculation method in this paper. It can be seen from Fig. 5 that the error of the calculated Bader charges increase gradually as the extraction of lithium or sodium ions increases.

For the majority of delithiation or desodiation processes, transition metal ions are traditionally thought to be the major active composition in the redox reaction processes. However, the present results show that redox reactions are always dominated by oxygen or sulfur ions in both the LiCrX2 and NaCrX2 (X = O and S) systems. For understanding the redox processes in Fig. 4, the spin-polarized partial density of states (PDOS) of Cr-3d and O-2p states for Li1−x/12CrO2 (with x = 0 and x = 1) are presented in Fig. 6a and b. It can be seen that LiCrO2 (x = 0) is a semiconductor, with all the electronic states of Cr and O ions occupied at the Fermi surface. However, for x = 1, some part of the Cr-3d and O-2p electrons are lost, some of the Cr-3d and O-2p states cross the Fermi surface which indicates the electron loss (electrons near the Fermi surface will be lost at first, but lost electrons are not limited only to those around the Fermi level). On the other hand, for Li1−x/12CrS2 (with x = 11 and x = 12) where PDOS are shown in Fig. 6c and d, results shows that the shifts of Fermi levels are very small for Li1−x/12CrS2, with x = 12 compared with x = 11. The loss of electrons in the Li1−x/12CrS2 systems are embodied in the whole energy region in the PDOS plot (see Fig. 6c). It should be mentioned that PDOS values in Fig. 6 are large, since they are contributed from all the atoms in the unit cell. Fig. 4 also indicates that charge transfer can happen from sulfur to chromium. Such “anomalously” charge transfer from anions to cations (O to Ru ions) have also been found in the first-principles calculations by Tarascon et al.,32 where the authors proposed a reductive coupling mechanism to explain the charge transfer from oxygen to metal ions. Summarizing, during the delithiation/desodiation processes, chromium ions lose electrons in oxides while gain electrons in sulfides, resulting from the weaker electronegativity of sulfur compared with oxygen.

From our electronic structure calculations, the Cr-3d and O-2p/S-3p states show significant overlaps, indicating that Cr and O/S orbitals possess strong hybridization. The redox processes can be understood through the energy levels of O/S (as well as Cr ions in the oxides) being pushed towards/cross the Fermi surface under strong p–d hybridization, leading to remarkably electron loss from the O/S energy levels. Such a picture explains the redox phenomenon in the LiCrX2 and NaCrX2 (X = O and S) systems. In addition, the coordination number around O/S ions decreases as the number of deintercalated lithium/sodium ions increases. More electrons might become unconstrained, resulting in larger DOS on the Fermi surface which might also be a reason to explain roughly the redox processes (Fig. 4) in the systems.

Fig. 6  The spin-polarized partial density of states (PDOS) for (a) Cr-3d states and (b) O-2p states, for Li1−x/12CrO2 (x = 0, 1); PDOS for (c) Cr-3d states and (d) S-3p states, for Li1−x/12CrS2 (x = 11, 12). The Fermi levels are represented by dashed lines.
Here, the spin-polarized band structures of the fully delithiated/desodiated phase CrO$_2$ ($x = 12$) are presented in Fig. 7. Comparing Fig. 7 with Fig. 2, we discover that when lithium ions are fully deintercalated, CrO$_2$ ($x = 12$) become a half-metal while LiCrO$_2$ ($x = 0$) is a semiconductor. From Fig. 2, it can be expected that, for the spin-up component, more and more bands around the Fermi level should become unoccupied due to the delithiation/desodiation, leading to half-metallic characteristics. Such a half-metallic character of CrO$_2$ has been well-studied in the literature. Comparison of charge densities for the Cr–O bond in LiCrO$_2$ and CrO$_2$ are also presented in Fig. 3a and 8. Fig. 8 reveals that the ionicity of the Cr–O bond for the fully delithiated phase is remarkably stronger than that of the fully lithiated phase. That is to say, the contours plots indicate that more significant loss of charges in CrO$_2$ can be found as compared with those in LiCrO$_2$, which is consistent with the analysis of Bader charges.

### 3.3 Magnetization

The magnetic moments could also help understand the redox reaction processes in these materials during the delithiation or desodiation processes. The calculated magnetic moments of Li$_{1-x/12}$CrX$_2$ and Na$_{1-x/12}$CrX$_2$ (X = O and S) at different lithium/sodium compositions are listed in Table 3. According to the crystal field theory, for a given octahedral MO$_6$ polyhedron, the five d-orbitals of Cr split into two sets with e$_g$ and t$_{2g}$ symmetries. The energy levels in t$_{2g}$ symmetry are comparatively lower than those in e$_g$ symmetry. The electronic configuration of Cr atom is 3d$^3$4s$^1$. Chromium atoms will lose their one 4s electron and two 3d electrons in the processes of forming the LiCrX$_2$ and NaCrX$_2$ (X = O and S), leading to the Cr$^{3+}$ and the electronic configuration of 3d$^4$ (resulting in an atomic magnetic moment of 3 $\mu_B$ of Cr$^{3+}$). Since all the Cr$^{3+}$, O$^{2-}$ and S$^{2-}$ have been shown to participate in the redox processes when lithium or sodium ions are gradually deintercalated, the magnetization of the systems might happen, at least at low temperatures. The total magnetic moments of the systems (per formula unit), magnetic moments of the chromium ions together with the absolute values of the total magnetic moments minus the magnetic moments of chromium ions (designated as $|D|$) are listed in Table 3. In this paper, we take $|D|/2$ as the magnetic moment per oxygen/sulfur ion (there are two O/S ions per formula unit).

From Table 3, we can notice that the changes of magnetic moments for oxides are quite different from those of sulfides, we therefore discuss them separately.

At first, during the delithiation or desodiation of oxides Li$_{1-x/12}$CrO$_2$ or Na$_{1-x/12}$CrO$_2$ (in the processes of redox reaction $x = 1, 3, 4, \ldots, 12$), the total magnetic moments per formula unit change from about 3 $\mu_B$ ($x = 0$) to about 2 $\mu_B$ ($x = 12$). We might expect that Cr ions (with local magnetic moment of 3 $\mu_B$) compensate one electron (for extraction of one Li/Na) to become a Cr ion with magnetic moment of 2 $\mu_B$, but this is not the case. Both the chromium and oxygen ions play important roles in the compensation processes during the extraction of lithium/sodium ions. For Cr ions, magnetic moments vary from about 3 $\mu_B$ ($x = 0$) to about 2.5 $\mu_B$ ($x = 12$), for O ions, on the other hand, magnetic moments vary from 0 $\mu_B$ ($x = 0$) to about 0.5 $\mu_B$ ($x = 12$), as shown in Table 3. The magnetic moments of Cr ions decrease almost linearly with the composition $x$, while those of O increase linearly with $x$, resulting in a total magnetic moment of 2.0 $\mu_B$ ($x = 12$) per formula unit, supposing that the directions of Magnetic moments of Cr and O are in opposite.

On the other hand, during the delithiation or desodiation of sulfides Li$_{1-x/12}$CrS$_2$ or Na$_{1-x/12}$CrS$_2$ (in the processes of redox reactions $x = 1, 3, 4, \ldots, 12$), the total magnetic moments of the
systems and magnetic moments of Cr, S ions are also presented in Table 3. The results show that sulfur plays a major role in the compensation processes during the extraction of lithium or sodium ions. The magnetic moment of S (two S ions per formula unit) changes from about 0.3 $\mu_B$ ($x = 0$) to about 0.6 $\mu_B$ ($x = 12$). Moreover, the variation of the magnetic moment of Cr is less than 0.2 $\mu_B$ throughout the entire redox processes. The magnitudes of the magnetic moments of Cr ions are all larger than 3 $\mu_B$, indicating the loss of electrons by Cr during the redox processes. These discussions are in very good agreements with our Bader charge analysis. The magnetic moments of Cr increase almost linearly with the composition $x$, while those of Cr almost keep unchanged, resulting in a total magnetic moment of 2.5 $\mu_B$ ($x = 12$) per formula unit, considering that the directions of magnetic moments of Cr and S are in opposite.

### 4. Conclusions

In summary, we have employed the first-principles methods within the density functional theory to study the Bader charge transfer, the structural properties, electronic structures and the magnetizations during the entire delithiation or desodiation processes. The calculation results indicate that both the anions and cations participate in the redox reactions when the lithium or sodium ions are extracted from LiCrX$_2$ or NaCrX$_2$ ($X = O$ and S). Compared with cations, the anions play prominent roles in the charge compensation processes. Moreover, the loss of electrons of S ions is visibly larger than those of O ions, which is consistent with their electronegativities. Besides, for sulfides (LiCrS$_2$ and NaCrS$_2$), chromium ions even gain a small portion of electrons instead of losing electrons, where the electrons gained by chromium ions are originated from the S-3p band. For the redox reactions involved, they can be understood through the energy levels of oxygen/sulfur ions (as well as chromium ions in the oxides) being pushed towards/cross the Fermi surface due to the strong p–d hybridization. The present work should help understand the cationic and anionic redox processes in these systems.

### Conflicts of interest

There are no conflicts to declare.

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