

## Abstract

### 論文の内容の要旨

論文題目 Exploration of high-voltage cathode materials based on cationic and anionic redox chemistry  
(カチオンおよびアニオンの酸化還元化学に基づく高電圧正極材料の開発)

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In this thesis, cathode materials for rechargeable batteries are explored from the viewpoint of cationic and anionic redox chemistry.

In Chapter 1, background and motivation of the present research are introduced. High material cost and low energy density of lithium-ion battery, which hinders further deployments of grid energy storages and electric vehicles, are the bottlenecks to overcome. First, to reduce the material cost, developing sodium-ion battery (SIB) is a promising strategy because sodium resources are more abundant and widely distributed in the earth than lithium resources. However, higher redox potential of  $\text{Na}/\text{Na}^+$  than that of  $\text{Li}/\text{Li}^+$  by 0.3 V often limits the operating voltage of SIBs, which requires high-voltage cathode materials. Phosphate-based cathode materials using high-voltage  $\text{Cr}^{4+}/\text{Cr}^{3+}$  redox reactions are investigated in Chapter 2–4. Second, an additional redox reaction of oxygen ions (oxygen redox) in the lithium-rich transition-metal layered oxides is of great interest to increase the energy density. However, a voltage hysteresis ( $>0.8$  V) of the charge/discharge processes reduces the energy efficiency, which hinders the practical use of oxygen-redox cathodes. Because operating potentials correlate to the electronic structures, the chemical states of oxidized oxygen ions are elucidated in Chapter 5.

In Chapter 2, the  $\text{Cr}^{4+}/\text{Cr}^{3+}$  redox reaction in NASICON-type  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  are explored for high-voltage sodium-ion battery cathode.  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  exhibits a reversible  $\text{Na}^+$  (de)intercalation at 4.5 V vs.  $\text{Na}/\text{Na}^+$  through the biphasic transition, whereas the capacity faded rapidly upon cycling due to an inherent instability of the charged phase.

In Chapter 3, Ti-substitution with Cr in NASICON-type  $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$  is conducted to realize the stable  $\text{Na}^+$  (de)intercalation using the  $\text{Cr}^{4+}/\text{Cr}^{3+}$  redox reaction.  $\text{Na}_2\text{CrTi}(\text{PO}_4)_3$  functions at 4.5 V vs.  $\text{Na}/\text{Na}^+$  with a capacity retention of 90.0% after 50th cycle. Less lattice volume change with smaller biphasic miscibility gap of  $\text{Na}_2\text{CrTi}(\text{PO}_4)_3$  should results in the improvement of cycle performance. Creation of  $\text{Cr}^{4+}$  and the ligand hole in O  $2p$  orbital contributes to the charge compensation for the  $\text{Na}^+$  deintercalation as demonstrated by X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD).

In Chapter 4, a combination of XAS, XRD, and density functional theory (DFT) calculation demonstrates a high operating potential of 4.7 V vs.  $\text{Na}/\text{Na}^+$  in  $\text{Na}_{3-x}\text{Cr}_2(\text{PO}_4)_2\text{F}_3$  ( $0 < x < 1$ ) on account of the reversible electron extraction/creation from/into the  $3d(t_{2g})\text{--O } 2p$   $\pi$ -type antibonding orbitals. Whilst further  $\text{Na}^+$  deintercalation ( $x > 1$ ) to form  $\text{NaCr}_2(\text{PO}_4)_2\text{F}_3$  above 5.0 V vs.  $\text{Na}/\text{Na}^+$  remains elusive, optimization of durable cell-components for high-voltage operation may enable more activity and greater reversibility. No energy-level increments by crystal field splitting and intra-orbital Coulombic penalty, combined with the introduction of electronegative  $\text{F}^-$  ions, yield a record high-voltage in early  $3d$  transition metal-based cathodes in  $\text{Na}_{3-x}\text{Cr}_2(\text{PO}_4)_2\text{F}_3$ , even with inherently higher  $d$ -electron energy levels owing to smaller nuclear charge. As a conclusion of Chapter 2–4, utilizing low-cost  $\text{Cr}^{4+}/\text{Cr}^{3+}$  ( $3d^2/3d^3$ ), instead of  $\text{Co}^{3+}/\text{Co}^{2+}$  ( $3d^6/3d^7$ ) or  $\text{Ni}^{3+}/\text{Ni}^{2+}$  ( $3d^7/3d^8$ ) redox couple, is worthwhile for the realizing the low-cost SIBs with high energy density.

In Chapter 5, both a nonpolarizing oxygen-redox reaction of  $\text{O}^-/\text{O}^{2-}$  and a polarizing oxygen-redox reaction of  $\text{O}_2^{2-}/\text{O}^{2-}$  in O2-type  $\text{Li}_{1.12-y}\text{Ni}_{0.17}\text{Mn}_{0.71}\text{O}_2$  are demonstrated. X-ray absorption/emission spectroscopy and magnetic measurements indicate the kinetic formation of  $\text{O}_2^{2-}$  from  $\text{O}^-$  through a square scheme. DFT calculations clarifies that  $\text{O}_2^{2-}$  formation is favorable when oxide ions suffer over oxidization. The kinetic  $\text{O}_2^{2-}$  formation explains the voltage hysteresis. These insights emphasize the importance of suppressing the formation of  $\text{O}_2^{2-}$  and maximizing contribution of the nonpolarizing  $\text{O}^{2-}/\text{O}^-$  redox couple to develop the energy-efficient oxygen-redox battery electrodes.

In Chapter 6, the conclusion of Chapter 2–5 and future perspectives are summarized. This thesis paves the way toward the developments of high-voltage cathode materials with low-cost and high energy density.