

ハロゲン化物イオン含有層状複水酸化物の アニオン電池用新規電極材料への応用

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Halide-layered Double Hydroxides as New Electrode Materials for Anionic Storage Systems

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In recent years, anion batteries in which anions intercalated during charging and discharging process have attracted attention as next-generation batteries. Current common cathodes based on halide or oxy-halide salts show limited electrochemical performances. Layered double hydroxide (LDH), represented by the general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2][A_{x/n}^{n-} \cdot m\text{H}_2\text{O}]$, has recently proposed as new cathode candidates. Intercalation of anion is expected through LDH structure. The driving force of anion mobility in halide-LDHs is expected to be promoted by the change of the transition metals ratio by electrochemical redox reactions. Cl-LDHs thin film coatings and powders were prepared and used to investigate the involved redox behavior and anionic batteries.

1. Introduction

The development of sustainable, efficient, safe, and cheap electrochemical energy storage is a widely recognized goal. Most electrochemical systems have focused on the cation transfer, so far. Anion batteries are taking attention as novel, sustainable, and safe electrochemistry with promising energy density properties (Figure 1, 2500 Wh L⁻¹).

Electrochemical anion storage behavior (e.g., F⁻, Cl⁻) was initially proved using metal halide or oxy-halide salts (e.g., FeCl₃, BiF₃, FeOCl) as cathodes (Figure 1). These cathodes show limited electrochemical performances because of severe volume changes during conversion reactions of halide anions transfer accompanied by an inevitable electrode deterioration upon cycling¹⁾.

Recently, halide layered double hydroxide (LDH)²⁾ has been proposed as a new cathode. In contrast to metal oxides or metal halide salts that use conversion reaction for the anion transport, halide anions can be intercalated into a halide-LDH structure²⁻³⁾, and therefore, their structural integrity is more stable upon cycling. However, the battery still shows low capacity and capacity fade. The chemical composition of the halide-LDH cathode is expected to be essential to achieve a superior energy density.

2. Experimental Section

LDH was deposited on ITO substrates by a sol-gel process and hot water treatment⁴⁾. LDHs powders were prepared by co-precipitation process and exchange process was carried out under immersion in NaCl/HCl solutions. The batteries were prepared by using an electrode sheet prepared by doctor blade process on aluminum foil, Li metal as a counter electrode, and a Bpy1,4Cl-propylene carbonate solution as an electrolyte. The electrochemical evaluation was performed by cyclic voltammetry (CV) measurement and battery charge/discharge measurements.

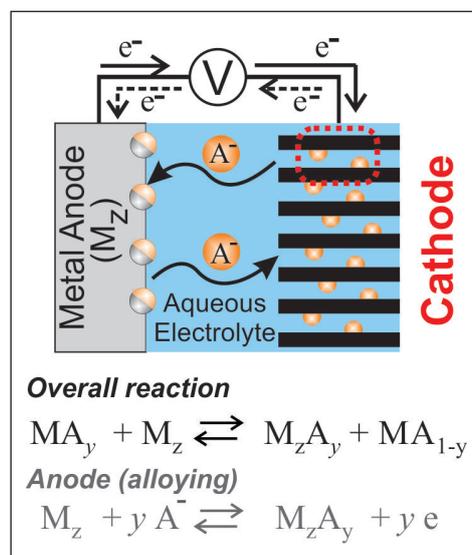


Fig. 1 Anion Secondary Batteries.

3. Result and discussions

LDH structure was confirmed in both, thin-film coatings and powders. The exchange process (CO^{3+} to Cl^- anions) was conducted in powder samples. The exchange conditions (NaCl/HCl solutions) lead to the detachment of the coating which suggests LDH exfoliation is also occurring in the powder samples. The LDH crystal phase after the exchange process does not show significant changes. The transition metals' valence also remains unchanged based on X-ray absorption measurements.

CV measurement of Cl-LDH thin film coatings shows a reversible electrochemical redox. The reversible redox was also confirmed in the change of the color film during CV measurement. For example, Cl-LDH containing Co displays electrochemical redox at 0.5 V (vs. Hg/HgO) with a reversible color change from purple (divalent Co) to green (trivalent Co). The electrochemical redox reactions prove that transition metals are active in the LDHs structure and able to promote the insertion and disinsertion of Cl^- ions.

CV measurement of Cl-LDH battery shows peaks at about 1.7 and 2.4 V (vs. Li / Li⁺). Contrary to CV measurement in Cl-LDH thin-film, the multiple peaks suggests that anion transport may occur in two-step (or more) reactions. Figure 2 (top) shows the charge/discharge profiles of Cl-LDH battery. The observed plateaus are in good agreement with CV. Figure 2 (bottom) displays presumable reactions with Cl-LDH containing Co, in which the partial disinsertion of Cl^- ions can occur. Further studies will be needed to clarify the mechanism of Cl^- ion transport. Specific capacity around 60 mAh g⁻¹ is obtained after 10 cycles.

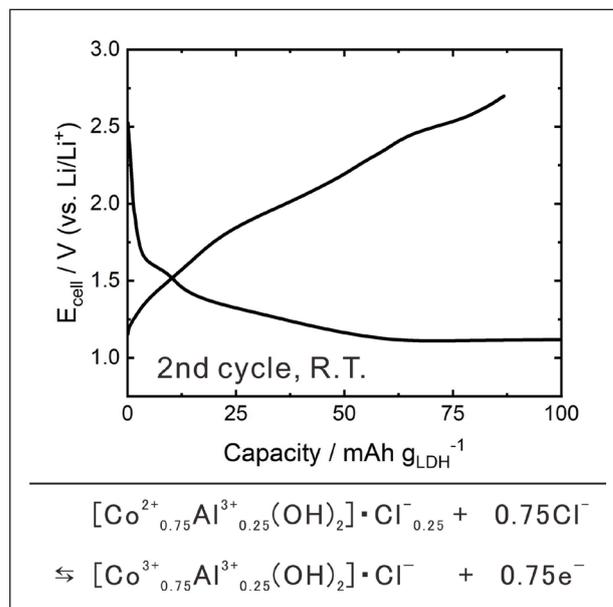


Fig. 2 Top: CV of Cl-LDH battery.

Bottom: Presumable reactions with LDH.

4. Conclusions

LDHs were investigated as candidates for application as cathodes in anion secondary batteries. Physicochemical characterization and electrochemical analyses were carried out to understand anion transport.

REFERENCES

- 1) *European Journal of Inorganic Chemistry*, (2017) 2784-2799.
- 2) *Journal of Materials Chemistry A*, **8** (2020) 12548-12555.
- 3) *Scientific Reports*, **9** (2019) 2462.
- 4) *Thin Solid Films*, **516** (2018) 4526-4529.