

# 論文の内容の要旨

## 論文題目 Cathode Materials for Rechargeable Magnesium and Lithium Batteries

(マグネシウム及びリチウム二次電池正極材料の開発)

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### 1 Background

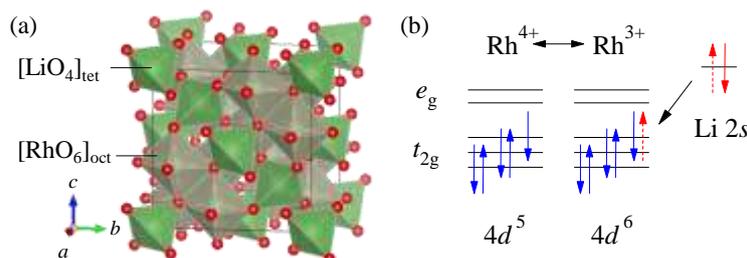
Insertion electrode materials are widely used in rechargeable batteries for electrical energy storage. Material research has been focused on the structural features of host materials to look for available void spaces for guest ions. However, electron transfer is always involved during the insertion, we suggest in this study that such an electronic process should be equally and worthy investigated.

### 2 A new "zero-strain" cathode material for lithium batteries

#### 2.1 Motivation and strategies to suppress the lattice strain in two-phase electrodes

The constant equilibrium voltage in a two-phase electrode merits for practical applications. But two-phase systems often suffer from slow  $\text{Li}^+$  kinetics and poor cycle performance. The so-called "zero-strain" material is one of the ideal systems with a small lattice mismatch, which is discussed to be an important factor for the enhancement of two-phase electrode performance.

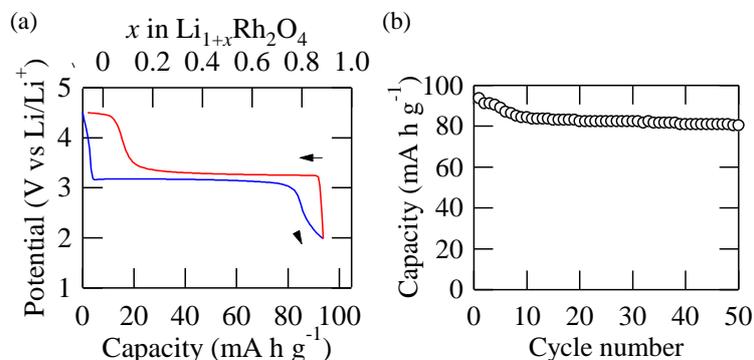
One of the major causes for the lattice mismatch is the Jahn-Teller effect, which is typically observed in the 3 V region of  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  by high-spin  $\text{Mn}^{3+}$ . For octahedral geometries of ligands as in spinel oxides, the Jahn-Teller effect is much smaller for  $t_{2g}$  electrons than for  $e_g$  electrons. We here propose that  $\text{Li}_{1+x}\text{Rh}_2\text{O}_4$  can be regarded as a new "zero-strain" system.  $\text{LiRh}_2\text{O}_4$  crystallizes in the spinel structure with low-spin  $\text{Rh}^{3+}$  and  $\text{Rh}^{4+}$  due to a large cubic crystal field and reduced Hund's coupling of  $4d$  orbitals (Figure 1). In  $\text{LiRh}_2\text{O}_4$ , the broad  $4d$  band is itinerant as compared with  $3d$ , and the Jahn-Teller transition is suppressed below room temperature.



**Figure 1** (a) The crystal structure of  $\text{LiRh}_2\text{O}_4$ . (b) Electron transfer in  $\text{Li}_{1+x}\text{Rh}_2\text{O}_4$ . Electrons flow from Li to  $t_{2g}$  orbitals of low-spin Rh ions.

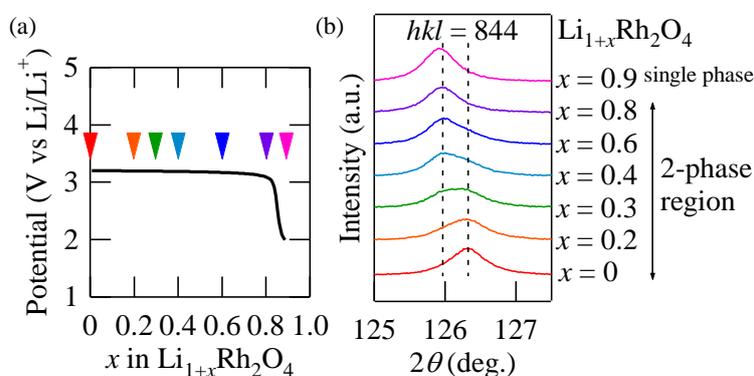
## 2.2 A small lattice distortion in $\text{Li}_{1+x}\text{Rh}_2\text{O}_4$ - The "zero-strain" behavior

The charge-discharge curve of  $\text{Li}_{1+x}\text{Rh}_2\text{O}_4$  exhibits a flat potential curve around 3.2 V (vs.  $\text{Li}/\text{Li}^+$ ), which might be a coexistence of two phases (Figure 2). The fine reversibility over 50 cycles implies that the discontinuous volume change of unit cells is rather small and the structural fatigue is suppressed.



**Figure 2** (a) The charge-discharge curve and (b) capacity retention of  $\text{Li}_{1+x}\text{Rh}_2\text{O}_4$ .

Structural analysis confirmed the coexistence of two phases (Figure 3): diffraction patterns around the 844 reflection within the flat potential range ( $0 \leq x \leq 0.8$ ) consist of two peaks centered at  $2\theta = 126.0^\circ$  and  $126.3^\circ$ . The volume change of  $\text{Li}_{1+x}\text{Rh}_2\text{O}_4$  is as small as *ca.* 0.5%, which is much smaller than other two-phase systems, such as  $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$  (*ca.* 5.6%) and  $\text{Li}_{1-x}\text{FePO}_4$  (*ca.* 6.8%), and is comparable to the so-called "zero-strain" material  $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$  (*ca.* 0.2%). We propose  $t_{2g}$  and itinerant character of  $d$  electrons involved in the two-phase reaction process as one strategy to design "zero-strain" systems.



**Figure 3** (a) Li insertion process and (b) X-ray diffraction patterns ( $hkl = 844$ ) of  $\text{Li}_{1+x}\text{Rh}_2\text{O}_4$ .

## 3 Materials of $d$ - $p$ orbital hybridization for magnesium batteries

### 3.1 Motivation and strategies to overcome barriers from the electronic point-of-view

Magnesium batteries promise to be safer and cheaper than lithium, and have potential higher storage capacity. But magnesium batteries have not yet been developed practically: (1) it is difficult to construct functional magnesium batteries because magnesium metal becomes inactive in most electrolytes; (2) strong Coulomb interactions between Mg ions and the local crystal structure result in slow  $\text{Mg}^{2+}$  diffusion kinetics; (3) only a few studies had been conducted and most of them showed that common lithium electrodes failed to reversibly host Mg ions.

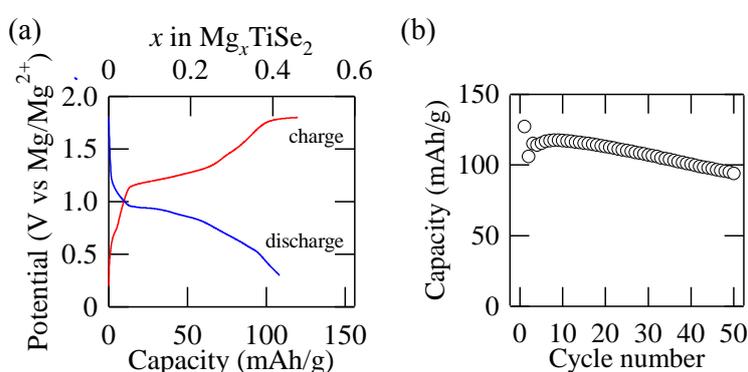
In  $\text{Mo}_6\text{S}_8$ , reversible Mg insertion has been reported to have easy charge redistribution in its cluster

structure:  $[\text{Mo}_6]$  clusters exchange electrons as a whole unit, but each Mo only changes slightly. However the number of cluster compounds is limited, thus other alternate materials with a similar electronic environment need to be developed. The valance change might be moderated by electron compensation from ligand anions, only if energy levels of  $d$  (metal) and  $p$  (anion) orbitals are close to each other. In a strongly  $d$ - $p$  orbital hybridized system, extended polyhedra of the central metal atom and surrounding anions can exchange electrons like "electronic clusters".

Titanium has been chosen for our candidate elements: (1) Ti  $3d$  is very close to  $p$  orbitals of sulfur and selenium; (2) Ti  $3d$  has a relatively high orbital level to address limitations of our electrolyte for a low operating potential; (3) titanium is the second most abundant element among transition metals. We here propose  $\text{TiSe}_2$  and  $\text{TiS}_3$ , both showed reversible charge-discharge reactions with higher or comparable capacities to  $\text{Mo}_6\text{S}_8$ .

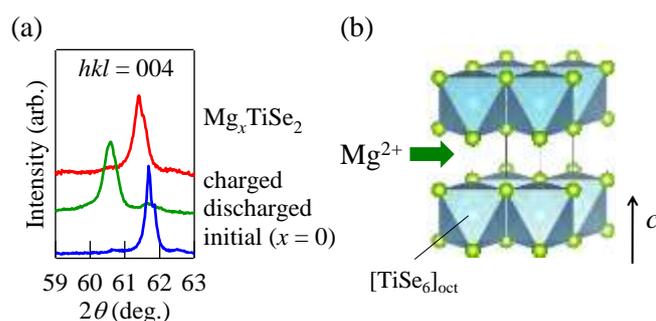
### 3.2 Enhanced electrode performance in $\text{TiSe}_2$ by itinerant $4p$ orbitals

$\text{TiSe}_2$  has a typical layered structure of dichalcogenides. It has metallic conductivity and hybridized  $d$  and  $p$  orbitals near the Fermi energy level, which is favorable for electrode applications. A specific capacity over 100 mAh/g (Figure 4), which is larger than  $\text{Mg}/\text{Mo}_6\text{S}_8$  (*ca.* 75 mAh/g), and reversible cycling of 50 cycles were obtained in  $\text{Mg}/\text{TiSe}_2$  cells. Compared with the capacity of  $\text{Mg}_x\text{TiS}_2$  (*ca.* 20 mAh/g), the enhanced performance of  $\text{Mg}_x\text{TiSe}_2$  might be attributed to Se  $4p$  orbitals because  $4p$  can extend further than S  $3p$  thus hybridizes more with Ti  $3d$ .



**Figure 4** (a) Charge-discharge curves and (b) capacity retention of  $\text{Mg}_x\text{TiSe}_2$ .

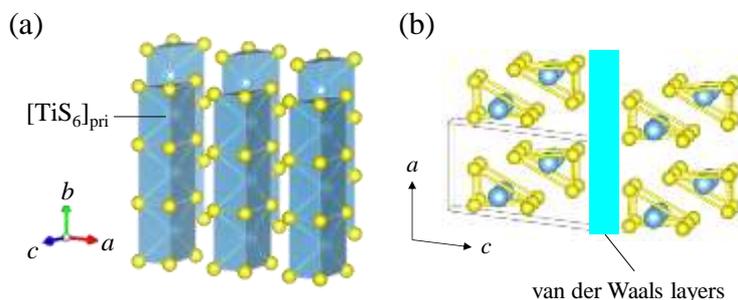
$\text{Mg}_x\text{TiSe}_2$  keeps its original layered  $\text{TiSe}_2$  structure during cycling. Reversible lattice expansion along the  $c$  axis was observed (Figure 5), which implies that Mg ions might be reversibly inserted into the vacant van der Waals layers perpendicular to the  $c$  axis.



**Figure 5** (a) X-ray diffraction patterns ( $hkl = 004$  reflection) of  $\text{Mg}_x\text{TiSe}_2$ . (b) The crystal structure of  $\text{TiSe}_2$  and the possible  $\text{Mg}^{2+}$  insertion process.

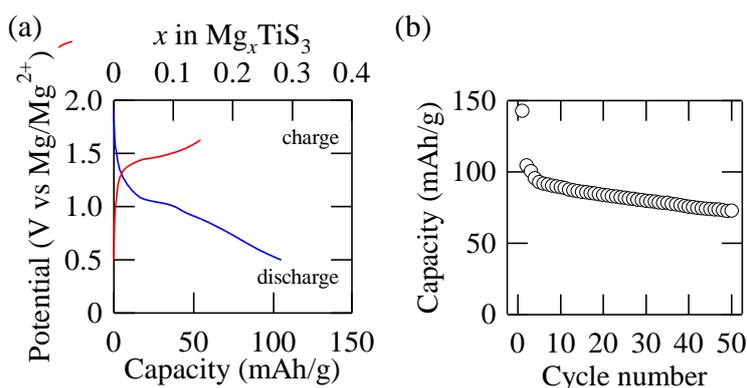
### 3.3 The possibility of high storage capacity in $\text{TiS}_3$

$\text{TiS}_3$  has a one-dimensional structure (Figure 6). It is a narrow-gap semiconductor with hybridized  $d$  and  $p$  orbitals, which is also considered suitable for electrode applications since conductivity might be enhanced during the insertion process.



**Figure 6** (a) The crystal structure of  $\text{TiS}_3$  (b) View of the van der Waals layers in  $\text{TiS}_3$ .

Electrochemical tests of  $\text{Mg}/\text{TiS}_3$  cells over 50 cycles obtained a specific capacity *ca.* 80 mAh/g (Figure 7) comparable to  $\text{Mg}/\text{Mo}_6\text{S}_8$ . Preliminary structural analysis shows that there is no conversion reaction during cycling.



**Figure 7** (a) Charge-discharge curves and (b) capacity retention of  $\text{Mg}_x\text{TiS}_3$ .

$\text{Mg}_x\text{TiS}_3$  has also been tested at a very slow rate (0.001 C) to investigate the possibility of large capacity, where a capacity of *ca.* 300 mAh/g was obtained. Further investigation should involve enhancement of electronic conductivity and downsizing particle sizes so as to optimize its high-capacity performance.