

## 博士論文の要約

論文題目 Electrochemical Modulation of Spin State and Magnetism for Geometrically Frustrated Magnetic Materials  
(電気化学的イオンドープがもたらすスピン・フラストレーション格子のスピン状態と磁性の変調)

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Geometrical frustration often leads to unimaginable magnetic properties for magnets, due to their vast degenerate ground state, such as spin glass, spin ice, and quantum spin liquid. Symmetry breaking provides an alternative pathway to understand the magnetism of frustrated magnets, as well as to achieve an unprecedented magnetic order out of the degenerated ground state. By using the solid-state electrochemical technique, the spin state, valence state, exchange interaction, and coordination environment of magnetic ions can be reversibly modulated. A comprehensive magnetic study of electrochemical intermediate phases may reveal the evaluation of magnetic properties and the mechanism of underlying magnetic ordering. Meanwhile, this magnetic study can help to identify the redox species, figure out the redox/degeneration mechanism, and develop advanced energy storage systems.

In Chapter 1, the concepts of geometrical frustration, some examples of frustrated lattices, and the possible magnetic ground states are first presented. I then discuss the origins of symmetry breaking, which is regarded as the driving force for magnetic ordering after electrochemical process. In the last section, I introduce some related work concerning the electrochemical modulation of magnetism and the magnetic monitoring of electrochemistry. To meet those strategies, two redox-active geometrically frustrated materials are selected as the target materials to carry out the electrochemical/magnetic measurements, i.e. 3D pyrochlore-lattice spinel  $\text{LiMn}_2\text{O}_4$  and 2D kagome-lattice copper tetrahydroxybenzene (CuTHQ) metal-organic framework (MOF).

In Chapter 2, the crystal structures of electrochemically induced  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $0.07 \leq x \leq 0.97$ ) are studied by the Rietveld refinements of powder X-ray diffraction patterns. A single cubic phase is confirmed in the  $\text{Li}_{0.93}\text{Mn}_2\text{O}_4$ , the  $\text{Li}_{0.50}\text{Mn}_2\text{O}_4$ , and the  $\text{Li}_{0.07}\text{Mn}_2\text{O}_4$  phases. DC magnetic susceptibility shows that antiferromagnetic superexchange interactions are dominant in all compounds. The strongly frustrated  $\text{Li}_{0.93}\text{Mn}_2\text{O}_4$  exhibits a cluster spin-glass transition at  $T_f=38$  K, while the weak frustrated  $\text{Li}_{0.07}\text{Mn}_2\text{O}_4$  is in a long-range antiferromagnetic order at  $T_N=30$  K, as evidenced by frequency-dependent AC susceptibility curves and a  $\lambda$ -type anomaly in heat capacity. Interestingly, a unique magnetic ground state of noncollinear antiferromagnetic order is found below  $T_m=16$  K for the intermediate phase  $\text{Li}_{0.50}\text{Mn}_2\text{O}_4$ , which is unveiled for the first time in the spinel  $\text{Li}_x\text{Mn}_2\text{O}_4$  system. Here, the Dzyaloshinskii–Moriya (DM) interactions in non-inversion symmetric  $\text{Li}_{0.50}\text{Mn}_2\text{O}_4$  phase are considered to be the origin of this nontrivial magnetic order.

In Chapter 3, highly crystallized CuTHQ MOF powder is synthesized by hydrothermal method. During the first discharge process, CuTHQ exhibits an unexpected capacity of 436 mAh/g, which exceeds the theoretical capacity of CuTHQ (259 mAh/g). Ex-situ electron spin resonance (ESR) spectra reveal that both Cu(II) and quinone group are redox-active, and the quantitative analyses of magnetic susceptibility suggest that Cu(II) can be reduced via a one-electron reaction to Cu(I); quinone group is only partly reduced to semiquinone. The extra capacity can be explained by the electrochemical absorption of  $\text{Li}^+$  via non-Faradic capacitance process, which is accompanied by filling electrons to the Fermi level and thus leads to the increasing of Pauli paramagnetism by two orders of magnitude. An anisotropic g-factor is detected for 2D CuTHQ MOFs, indicating the axially symmetric coordination environment in the CuTHQ complex. It should be noted that as-prepared CuTHQ shows no magnetic ordering down to 2 K, despite a Weiss temperature of  $\theta=-20$  K, which suggests a promising quantum spin liquid candidate of CuTHQ.