



The goal of the Laboratory for Energy Storage and Conversion (LESC), at the University of California San Diego Nanoengineering department, is to design and develop new functional nanomaterials and nanostructures for advanced energy storage and conversion applications. Prof. Shirley Meng, an affiliated faculty member with CMRR, is leading her group to design, optimize and develop new materials for energy storage for electric vehicles and smart grids, as well as permanent magnetic materials for electric driving motors and wind turbines. Meng's group research focuses on the direct integration of novel experimental techniques with first principles computation modeling methods for rational materials characterization and design.

Choosing the best cathode material used in a Li-ion battery is one of the most crucial issues in achieving higher energy densities, since the energy density is directly correlated to the specific capacity associated with that cathode material. The conversion type materials have been studied as potential electrode materials for higher energy lithium ion batteries (at least double the energy density of today's technology). We have investigated the NiF₂ based conversion materials and the conversion reaction includes the nucleation and growth of nanosized Ni particles. In order to understand the conversion mechanism more thoroughly, we utilized a Superconducting Quantum Interference Device (SQUID) magnetometer, which is a powerful technique for detecting nanosized magnetic particles such as Ni nanoparticles that otherwise could be missed by diffraction based analytical techniques.

As shown in Fig. 1, the magnetic hysteresis loops were obtained at 5 K, since the material is in a superparamagnetic regime. Superparamagnetism is a form of magnetism, which appears in small ferromagnetic or ferrimagnetic nanoparticles. In sufficiently small nanoparticles (<10nm), magnetization can randomly flip direction under the influence of temperature. When the time used to measure the magnetization of the nanoparticles is much longer than the Néel relaxation time, their magnetization appears to be in average zero; they are said to be in the superparamagnetic state. On the other hand, the magnetic moments remain at a fixed direction during a single measurement when the temperature is lower than the blocking temperature (T_B), where the ferromagnetic moment becomes superparamagnetic. The distinguishable magnetic hysteresis was observed at 5K since NiF₂ was mostly converted to nanosized-Ni particles by the conversion reaction. It is also suggested that the conversion reaction in NiF₂ is very slow, which contributes to the formation of extremely small particles. These nanoparticles are not precisely detected by diffraction techniques due to the nanosize peak broadening.

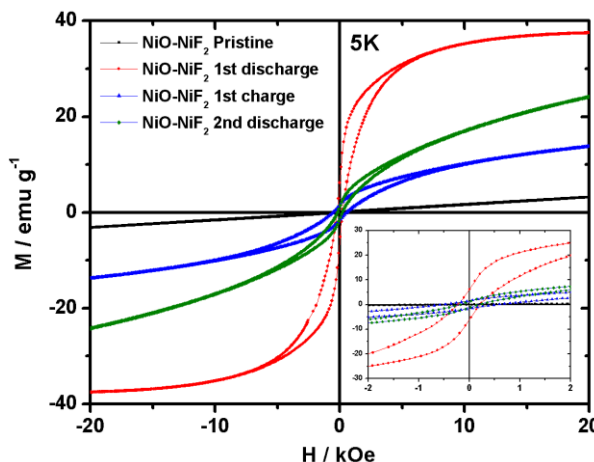


Fig. 1. Magnetic hysteresis of NiO-doped NiF₂ conversion materials

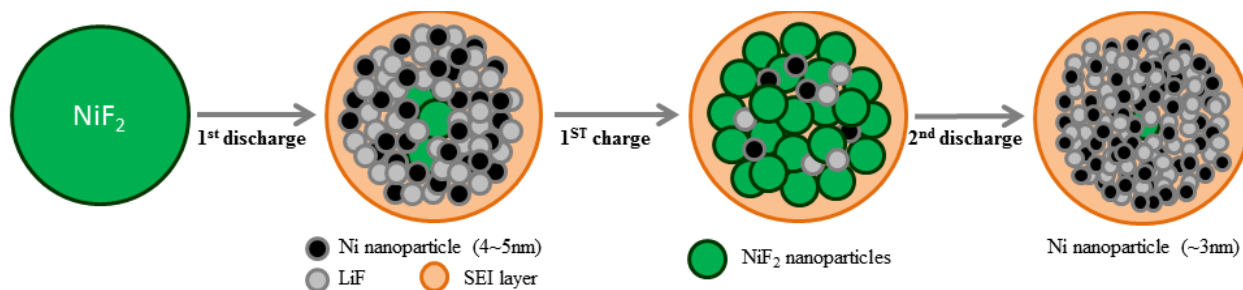
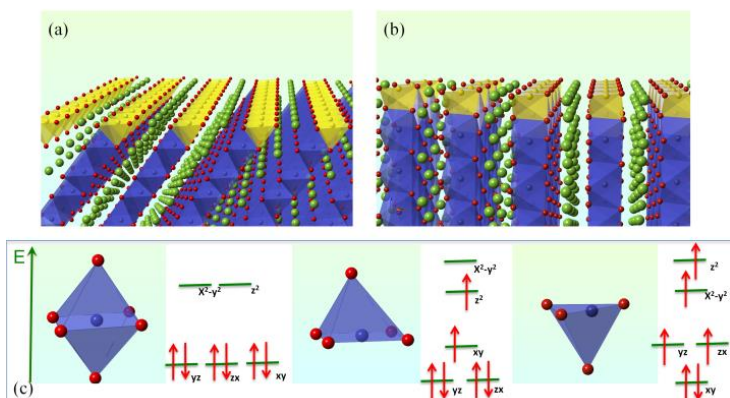


Fig. 2. Schematics illustrating the possible conversion mechanisms occurring in NiF₂

Based on the SQUID analysis, we could propose the possible conversion mechanisms occurring in NiF₂. The magnetic measurements provided more fundamental understanding on the phases including the size information on nanosized-Ni particles during the conversion reactions. This work is published in **Electrochimica Acta** 2012, 59, 213 by Ph.D. candidate Daniel Lee and colleagues.

Meng's group also recently reported the low coordinated geometries on the surface of the oxides can result in spin states that are distinct from the bulk. Consequently, unique magnetic and electronic properties arise and alter the materials performance in devices. Lithium cobalt oxide (LiCoO₂) is a compound of great technological importance, as it has been the most widely used positive electrode material for lithium ion batteries for nearly two decades. In recent years, it has been demonstrated that ultra fast charge/discharge rate capabilities can be achieved in this compound when nano-scale (< 50nm) particles with morphology optimal for Li intercalation are prepared and tested. We presented in this work that this can similarly be explained by the presence of intermediate spin (IS) or high spin (HS) Co³⁺, a phenomenon which alters the lithium (de)intercalation voltage significantly.

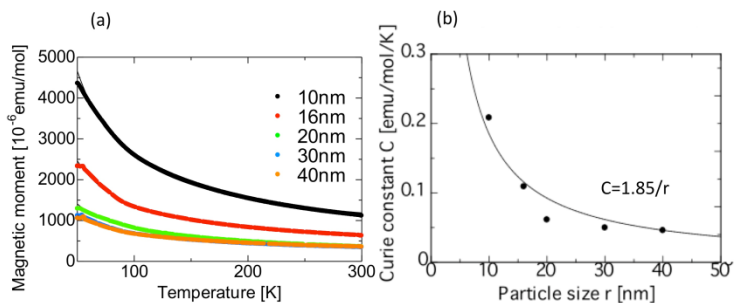


In bulk LiCoO₂, Co³⁺ has six 3d electrons, while in octahedral oxygen environment; it would split into t_{2g} and e_g orbitals, which are d_{xy}, d_{yz}, d_{xz} and d_{x²-y²}, d_{z²} respectively. It has been found by previous studies that in bulk, Co³⁺ is in the low spin (LS), where all the electrons are paired in t_{2g} orbitals, as shown in Left Figure (c). On the {104} surface, the Co³⁺ ions are coordinated by five oxygen ions, resulting in a square pyramidal

configuration. With first principles calculation, we found that the surface energy is lowered significantly when going from the LS configuration (1118mJ/m²) to the IS (312mJ/m²), which has two unpaired electrons. On the {110} surface, the Co³⁺ ions on the surface are coordinated by four oxygen ions with a pseudo-tetrahedral configuration. The surface energy is minimized from 2227mJ/m² (LS) to 1241mJ/m² (HS), which has four unpaired electrons.

Magnetic measurements were performed, using a superconducting quantum interference device (SQUID) at CMRR, at a magnetic field of 1.0 T in the temperature range of 5-300K. The molar magnetic susceptibility of the various sized nano-LiCoO₂ particles are plotted as a function of

temperature in Right Figure. The magnetic susceptibility of bulk LiCoO_2 is very low, which is attributed to the LS Co^{3+} in the layered structure. The magnetic susceptibility increases with the decrease in size, which is contributed from the unpaired electrons on the surface. This work is recently published by Ph.D. candidate Danna Qian and colleagues in **Journal of the American Chemical Society**, 2012, 134(14), 6096.



Rare earth permanent magnets are key components in electric vehicle motors and in wind turbine electricity generators, and there is a growing international concern over the economics of rare-earth raw materials. DOE is addressing the issue from the technology side through its **ARPA-E** program, REACT—Rare Earth Alternatives in Critical Technologies—whose mission is to develop substitute materials for rare earth permanent magnets. Meng and her postdoc Dr. Kyler Carroll are teaming up with Virginia Commonwealth University to demonstrate a new class of permanent magnets based on a carbide-based composite magnet. For understanding the fundamental mechanism behind the high magnetic energy in these type of carbide composite, Meng's group have to carry out advanced characterization techniques such as synchrotron X-ray absorption spectroscopy (XAS) in order to understand the local structures of metal – carbon atomic structures. In the picture, the student Ph.D. candidate Michael Verde visited the facility for the first time and is mesmerized by the sophisticated experimental setup at Brookhaven National Laboratory Beam line X18B.



For more information about the Laboratory for Energy Storage and Conversion (LESC) and Prof. Shirley Meng's research group, please visit <http://ne.ucsd.edu/smeng/>