Combined computational and experimental NMR analyses on $Na_{2-x}RuO_3$

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Utilization of oxygen redox is a possible strategy to achieve larger capacity in cathode materials. Recent studies have shown that oxygen redox is often triggered in Li/Na-excess cathode materials $A_{1+y}M_{1-y}O_2$ (A=Li, Na, M=transition metal),[1,2] however detailed analyses have been hindered due to the irreversible structural disordering upon first charging process. We have shown that honeycomb ordered Na_2RuO_3 ($Na_1[Na_{1/3}Ru_{2/3}]O_2$) can be a model system with its unique property of progressive structural ordering upon charging, leading to a highly reversible oxygen redox reaction (Figure 1a).[3]

We applied ^{23}Na nuclear magnetic resonance (NMR) spectroscopy for the characterization of local environments of $Na_{2-x}RuO_3$ with combined computational and experimental approaches. Here, we calculated the Fermi contact shift caused by paramagnetic electrons,[4] which dominates the signal in the present system. The DFT calculations were performed using VASP Software with PAW method and PBE functional. Ferromagnetic ordering was considered for all the calculations. ^{23}Na NMR signals were recorded at 500 MHz (single pulse) at spinning rates of ν_R = 30 KHz.

In Na_2RuO_3, ^{23}Na NMR signals are observed at 2400 ppm and 877 ppm. Each signal was assigned to three crystallographic Na sites (Figure 1b) of which Fermi contact shifts were calculated to 4330, 1489 and 1329 ppm by DFT, respectively. Such large peak shift is due to the paramagnetic character of Ru(IV) ions and is proportional to the spin density at the nucleus of Na ions. On the contrary, less shifted signals at 150 ppm and 0 ppm are observed in $NaRuO_3$. The density of states calculations also confirmed the paramagnetic character in Na_2RuO_3 and the absence of magnetism in $NaRuO_3$. Origin of the disappeared magnetism upon charging Na_2RuO_3 to $NaRuO_3$ will be discussed in the poster.

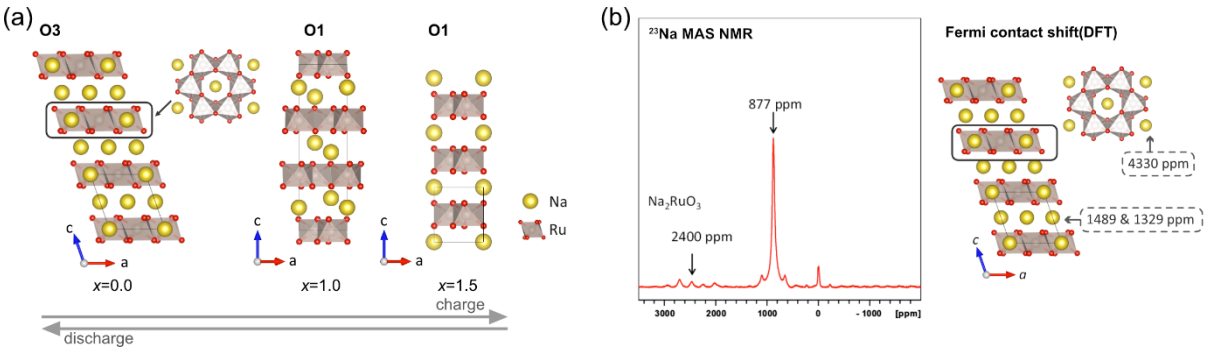

Figure 1. (a) Structure of $Na_{2-x}RuO_3$ and
(b) ^{23}Na NMR signals and DFT-based Fermi contact shift on Na_2RuO_3

References:
[1] P. Rozier et al, *J. Electrochem. Soc.*, **162** A2490 (2015)
[2] M. Okubo et al, *Chem. Mater.*, **9** 36463 (2017)
[3] B. Mortemard de Boisse et al, *Nature Comm.*, **7** 11397 (2016)
[4] D. Carlier et al, *Phys. Rev. B*, **67**, 174103