NMC Positive electrode materials with metal-site vacancies for Lithium-ion batteries

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One of the key issues with Li-rich NMC positive electrode materials is their high first-cycle irreversible capacity loss (IRC), which is usually around 20 % of their first charge capacity. Recently Li-rich positive electrode materials that can simultaneously exhibit low-IRC (~ 10 % or less) and high reversible capacity (> 240 mAh/g) have been reported [1]. The low-IRC materials were single phase layered materials that had inherent metal-site vacancies, determined by He pycnometry, in their pristine state. About 35 samples that can accommodate metal-site vacancies in their pristine state were synthesized and their IRCs were measured. Figure 1 shows a plot of % IRC and reversible capacity against the fraction of metal-site vacancies per formula unit. Low-IRC behaviour is well correlated to the concentration of metal-site vacancies of the studied materials [2]. ^{7}Li NMR experiments, which measure the distribution of Li between Li and transition metal layers, were performed on the pristine single-phase low-IRC materials. Correlations between the stoichiometry, vacancy content and the Li atom distribution allow a hypothesis for the mechanism behind low irreversible capacity to be developed.

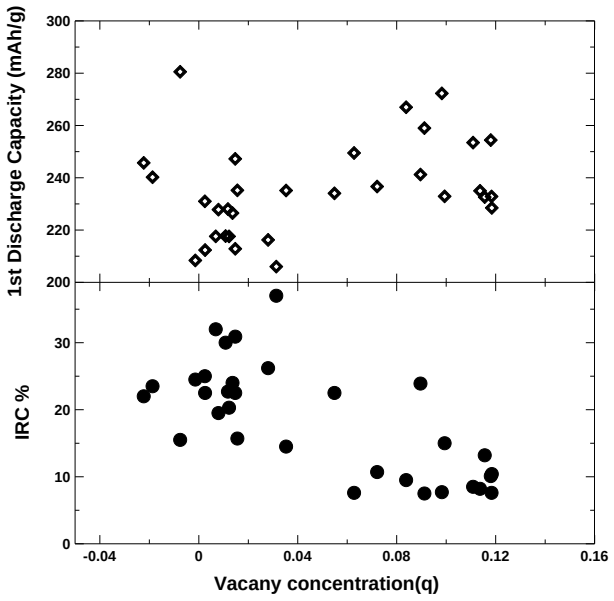

Figure 1. Reversible capacity (top panel) and fraction of irreversible capacity (bottom panel) of $Li_p\square_qNi_xMn_yCo_zO_2$ as function of vacancy content, q.

References:

[1] R. Shunmugasundaram, R. Senthil Arumugam, J. R. Dahn, Chem. Mater., **2015**, *27* (3), pp 757–767

[2] R. Shunmugasundaram, R. Senthil Arumugam, Kris Harris, Gillian Goward, J. R. Dahn submitted to Chem. Mater.