



Contribution ID: 47

Type: Poster

Superstructure-Suppressed Oxygen Evolution in Co-free Materials for Na-ion Batteries

Wednesday, November 29, 2023 5:50 PM (2h 10m)

Sodium-ion batteries have attracted great interest because of the wide range of their potential applications and sodium abundance. To make Na-ion batteries competitive, the research on Na-ion batteries focuses on the development of new electrode materials, offering higher specific charges and voltages to reach higher energy density and performance comparable to or higher than those of state-of-the-art Li-ion batteries [1]. Therefore, we are searching for novel Na-ion Co-free materials with high specific charge, preferably mainly based on earth-abundant elements like Mn. One promising approach to achieve this goal is the substitution of one of the transition metals by lithium, which not only increases energy density due to its low molar mass but also, as an additional positive ion in the structure, leads to the increase of manganese oxidation state. In conventional intercalation cathodes, Na-ions can move in and out of a layered material, with the charge being compensated by reversible reduction and oxidation of the transition metal ions. Since Mn⁴⁺ ions are not likely to change their oxidation state in the cycling voltage range, the anionic redox reaction on oxygen is likely to be the only accountable resource for the observed reversible capacity. This can increase the battery's energy density by storing charge on both the oxygen and manganese, rather than on the transition metal alone.

The aim of this work was to study the influence of the degree on charge compensation mechanism, crystal structure, and gas evolution in Mn-based materials, Na_{0.6}Li_{0.1}Mn_{0.9}O₂ and Na_{0.6}Li_{0.2}Mn_{0.8}O₂. To achieve this goal, materials have been synthesized using solid-state synthesis approach and characterized using electrochemical methods, operando XRD, Online Electrochemical Mass Spectrometry (OEMS) and X-ray Absorption Spectrometry (Swiss Light Source, SuperXAS beamline).

Na_{0.6}Li_{0.1}Mn_{0.9}O₂ showed an excellent initial capacity of 180 mAh/g, and the evolution of oxygen at high voltages during first charge was suspected from the shape of the potential profile. No particular Li ordering has been observed for this material. Na_{0.6}Li_{0.2}Mn_{0.8}O₂ had ribbon-type Li ordering [2] and a lower capacity of 140 mAh/g without showing any oxygen evolution characteristics in the potential profile.

The material with lower lithium content exhibited also an irreversible phase transition during first charge as detected by operando XRD. The gas evolution at voltages above 4.2 V suggests that irreversible oxygen redox reactions actually take place in case of Na_{0.6}Li_{0.1}Mn_{0.9}O₂. Additionally, XAS measurements revealed rather a peculiar behavior of the Mn oxidation degree upon first charge for this material. The decrease of the oxidation state of the transition metal at voltages seems to correspond well with the irreversible oxidation of O²⁻ ions and loss of oxygen from the structure during the first cycle, which was confirmed by OEMS. Furthermore, the presence of Li-ordering appears to stabilize Na_{0.6}Li_{0.2}Mn_{0.8}O₂ both in terms of crystal structure and gas evolution. The influence of different degrees of Li substitution in sodium manganese layered oxides on oxygen redox activity will be discussed.

Acknowledgements: The SCCER HaE network is acknowledged for funding

[1] S. F. Schneider, C. Bauer, P. Novák & E.J. Berg, *Sustain. Energy Fuels* 3 2019 3061

[2] R. A. House, U. Maitra, M. A. Pérez-Osorio, J.G. Lozano, L. Jin, J. W. Somerville, L.C. Duda, A. Nag, A. Walters, K-J Zhou, M. R. Roberts & P. G. Bruce, *Nature* 577 2020 502

Primary author: KONDRACKI, Lukasz (Paul Scherrer Institute)

Co-authors: Mr STROPP, Julian (Paul Scherrer Institute); Mr STEINER, Samuel (Paul Scherrer Institute); Dr WIERZBICKI, Dominik (Paul Scherrer Institute); Dr WACH, Anna (Paul Scherrer Institute); Dr TRABESINGER, Sigita (Paul Scherrer Institute)

Session Classification: Happy Hour and Poster Session