Helmholtz - OCPC - Programme 2017-2021

for the Involvement of Postdocs in Bilateral Collaboration Projects with China

PART A

Title of the project: Lithium/oxygen-insertion-induced structural evolution during synthesis of Li-containing oxides for next-generation lithium-ion batteries

Helmholtz Centre and institute:

Karlsruhe Institute of Technology (KIT), Institute for Applied Materials - Energy Storage Systems (IAM-ESS)

Project leader:

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Description of the project (max. 1 page)**:**

High-energy cathode materials for next-generation lithium ion batteries (LIBs) are crucially required for the application in large-scale energy storage and conversion devices.[1] Nowadays, some Li-containing 3*d*-transition-metal (TM) oxides (LTMOs) such as $LiCoO_2$, $LiMn_2O_4$ and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ have been successfully used as cathode materials for LIBs. Unlike these traditional oxides, in which the storage capacity is dependent on the cationic redox processes, the redox reaction of both TM and oxygen in Li-excess oxides could allow storage/release of a relatively large amount of lithium ions and electrons, and hence resulting in a pronounced improvement in the capacity.[2-3] For instance, a new disordered rock-salt (space group: $Fm\bar{3}m$) Li-excess $Li_4Mn_2O_5$ was reported to exhibit a high discharge capacity approaching 350 mAh g^{-1} between 1.2 and 4.2 V,[4] which is two times higher than that of currently used cathodes. Development of LTMOs with high-performance, therefore, quickly become essential. Unfortunately, unveiling the formation mechanism of LTMOs poses huge challenge because it is difficult to obtain information about the local structures and electronic states of lithium and oxygen in the formed oxides during high-temperature solid-state reaction.

Very recently, we demonstrated the experimental determination of lithium and oxygen incorporation into the host matrix of a spinel precursor during formation of monoclinic layered $Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O_2$.[5] With an increase in heating temperature, both lithium and oxygen successively enter into the spinel framework formed from precursor, thus gradually causing the generation of a rock-salt-type phase ($Fm\overline{3}m$) and finally resulting in the formation of a Li-rich layered phase ($C2/m$). However, the pressing open questions in the field of solid-state chemistry needed to be addressed are: (i) how and where is oxygen incorporated into the host architecture during high-temperature reaction? (ii) what is the driving force for TM migration and where do they move during lithium ion insertion into the bulk structure of the oxides?

The objective of this project is to explore the cleavage and formation of the chemical bonds (i.e. Li-O & TM-O bonds) in the reaction pathway of LTMO formation and figure out the rate-limitin step during high-temperature reaction. To achieve this goal, the above identified challenges will be solved experimentally as follows:

(i) A combination of *in situ* high-temperature synchrotron radiation diffraction (SRD), pair distribution function (PDF) and X-ray absorption spectroscopy (XAS) techniques will be performed to investigate the structural and electronic evolution of a mixture of the precursor together with lithium source such as Li_2CO_3 and LiOH;
(ii) Scanning/Transmission electron microscopy (SEM/TEM) and energy dispersive X-ray spectroscopy (EDX) characterizations will be used to study the morphological evolution and transition metal migration;
(iii) ^{7}Li magic-angle spinning nuclear magnetic resonance (MAS NMR) and inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements will be applied to determine the local environment of lithium cation and the chemical composition of compounds.

Lastly, the fatigue mechanism of cathode materials during operation in complete battery cells will be studied on the basis of uncovered formation mechanism.

References:
[1] A. Singer, et al, *Nat. Energy*, 2018, 3, 641. [2] M. Sathiya, et al, *Nat. Mater.*, 2015, 14, 230. [3] S. Hy, et al, *J. Am. Chem, Soc.*, 2014, 136, 999. [4] M. Freire, et al, *Nat. Mater.*, 2016, 15, 173–177. [5] W. Hua, et al, *Adv. Energy Mater.*, 2019, 20183094.

Description of existing or sought Chinese collaboration partner institute (max. half page)**:**

Sichuan University - School of Chemical Engineering

The Chinese partner at School of Chemical Engineering at Sichuan University (SCU) has a wide expertise in the development of advanced electrode materials for Li/Na-ion batteries. A platform for creative and comprehensive design experiments was established at Prof. Benhe Zhong's group, including a series of continuous stirred tank reactors for mass production of cathode materials, cylindrical battery processing facilities, glove boxes for battery construction, advanced battery test systems. The collaboration with SCU, started at the end of 2016, is based on our common interest in preparing new cathode materials for Li/Na-ion batteries. Up to now, we already have several joint papers published in high-ranked journals like *Advanced Energy Materials*, *Advanced Science*, *Journal of Materials Chemistry A*. The proposed work will allow for both KIT and SCU to be actively involved in the collaboration to answer the critical questions mentioned above.

Required qualification of the post-doc:

- PhD degree in chemistry, chemical engineering, material science or a closely related area.
- Experience with material synthesis, synchrotron radiation diffraction, electron microscopy, and neutron scattering techniques;
- Ability to writing scientific articles and effective communicating;
- Additional skills in analyzing neutron/X-ray powder diffraction data through Rietveld refinement will be a significant plus;

PART B

Documents to be provided by the post-doc, necessary for an application to OCPC via a postdoc-station in China, which is affiliated to a research institution like a university:

- Detailed description of the interest in joining the project (motivation letter)
- Curriculum vitae, copies of degrees
- List of publications
- 2 letters of recommendation
- Proof of command of English language

PART C

Additional requirements to be fulfilled by the post-doc:

- Max. age of 35 years
- PhD degree not older than 5 years
- Very good command of the English language
- Strong ability to work independently and in a team

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