Unraveling the original dissolution mechanism of LiFePO4 when treated for recycling

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Background incl. aims
This presentation aims at demonstrating the original mechanism involved during the acid leaching treatment of the very common material used in Li-ion batteries, LiFePO4. Such treatment is the basis of the hydrometallurgical process used for recycling the material and the understanding of the chemical reactions involved is critical to optimize the recycling process. To date and to our knowledge, such a mechanism established thanks to advanced TEM experiments among which operando liquid TEM and STEM EELS for phase mappings has never been highlighted.

Methods
We first carried out operando liquid TEM experiments to follow the evolution of the shape of the particules and to see if the dissolution process was monotonous or composed of severals growth and dissolution steps. Ex situ characterisations on materials residues recovered from partial dissolutions, including HRTEM imaging and STEM-EELS experiments, were then performed. They enabled the identification of the phases and their localisation. All the results are finally correlated and confronted to global chemical and structural analyses by the means of ICP-MS and XRD experiments.

Results
Operando liquid TEM experiments are demonstrating a monotonous dissolution process without any reprecipitation or growth of particles. Moreover as already reported by us [1], it was possible to show the kinetic observed operando was comparable with the one deduced from ex-situ dissolution experiments. Ex-situ XRD analyses are evidencing a rather quick formation of crystallites composed by the FePO4 phase with still the presence of the pristine LiFePO4 one. Discriminating both phases is a challenge but STEM-EELS and HRTEM analyses enabled to prove the coexistence of both phases into the same particles and they demonstrate that a core-shell type or shricking-core mechanism does not occur as it is usually observed during such reactions.

Conclusion
During this talk we are presenting the original dissolution mechanism that is based on the tranformation from monocristalline LiFePO4 particles toward polycrstalline FePO4 ones separated by LiFePO4 residues. We demonstrate the evolution occurs into the same particules without any nucleation of new particules. Then, this is the level of pH that is governing the continuous dissolution process or its interruption. This study is of importance since it allows process optimization. It is also of great interest on a fundamental aspect since we demonstrate the generation of particles where the LiFePO4 and FePO4 phases coexist. Such phenomenon is not really expected when we know the bahavior of the material that is always presenting monophased particles when used in a li-ion battery [2,3].

Keywords:

Operando-liquid-TEM, HRTEM, EELS, LiFePO4.

Reference:

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