Abstract #899, 224th ECS Meeting, © 2013 The Electrochemical Society

Application of the methodology of Design Of Experiments to the development of Li-Ion battery active materials

Sebastien Martinet, C. Bourbon, M. Amuntencei, D. Peralta, L. Simonin, M. Rey-Chapuis, S. Patoux

Commissariat à l'Energie Atomique et aux Energies Alternatives,
CEA-LITEN, Laboratory of Materials for Batteries

17 Rue des Martyrs, F-38054 Grenoble Cedex 9, France

1. Introduction

In the search for high energy cathode materials for Li-ion batteries, iron-substituted lithiated phosphate materials with the general formula $LiFe_xM_{1-x}PO_4$ (with $0 \leq x < 1$ and M= Mn, Co, Ni or a mixture of them) and so-called lithium rich lamellar oxides raise high interest. The phosphate compounds present the same olivine structure as the well-known $LiFePO_4$, and can deliver a theoretical capacity around $170mAh.g^{-1}$. The partial or global substitution of iron leads to higher potential than 3.45V vs. Li^+/Li, up to 4.1V for a full substitution of iron by manganese, for instance. The choice of the substituent(s) and the atomic ratio is opening a wide panel of cathode materials with different electrochemical performances. Although the lithium-rich compounds present very high practical capacity compared to the conventional layered oxides, they suffer from several practical limitations, such as the voltage decay upon charge/discharge cycling, the poor performances at high current rates, and the unusual high first cycle irreversibility.

To reach the sufficient level of performances for a practical application, there is clearly a need for developing and improving these two families of compounds with two different approaches: i) optimizing the elemental composition of the active material (choice and ratio of the different transition metal elements for instance), ii) optimizing the multi-parametric synthesis conditions.

2. Description of work

In this work, we will present 2 examples of the benefits that design of experiments (**DOE**) methodology may provide to Li-Ion battery material development such as: i) reducing significantly the number of experiments, ii) taking into account interactions between input parameters.

2.1 Mixture Design applied to Mixed Phosphate compounds

As the total substitution of manganese for iron is damaging the electronic conductivity of the phosphate [1], the optimization of the ratio of the different transition metal elements is of high importance to maintain sufficient electrochemical performances.

Recently, we investigated the preparation of mixed phosphates (Fe, Mn, Co and a “dopant”, including a maximum of 1/3 of iron) by an all-solid state route, benefiting from our past experience on $LiFePO_4$, and using DOE to minimize the number of compositions. Thanks to the adaptation of synthesis parameters, pure compounds were successfully obtained. A mixture design has been defined and run with 21 compositions in the selected domain. The impact of all the screened compositions with different degrees of substitution will be evaluated on the capacity and relative energy of materials. These results will be discussed, and will highlight the benefits of the DOE methodology. These data will be linked to cyclic voltammetry and electronic impedance spectroscopy (EIS) measurements with determination of electrochemical parameters.

2.2 Surface Response Design applied to Synthesis Conditions of Li-Rich Lamellar Oxides

The second example of the use of DOE concerns the optimization of the coprecipitation synthesis conditions to prepare LNMO lithium-rich lamellar oxide (Ni and Mn based, without Co). In that case, a surface response design has been defined with 6 input parameters corresponding to the main synthesis parameters.

The DOE has been analyzed through more than 20 outputs, both electrochemical and physical ones, such as discharge capacity at various rates, irreversible capacity, tap density, and so on. This work allowed us determining the main influence of the input parameters on each studied output. We finally used a multiparameter optimization to obtain the best compromise for the material performances (discharge capacity, tap density and others). In figure 1, one can see the increase of the discharge capacity from less than 210mAh/g for the initial synthesis conditions to more than 240mAh/g for optimized conditions, stable for 40 cycles. Further work is ongoing to increase once again this capacity and data will be presented at the meeting.

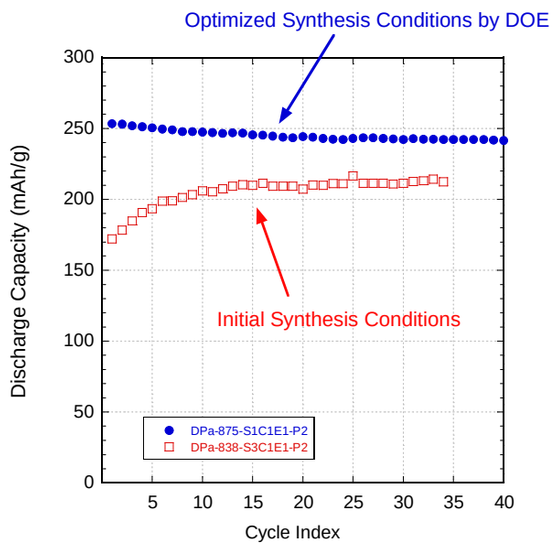

Fig. 1. Li-rich Lamellar Oxide LNMO discharge capacity at C/10 rate as a function of cycle number. Red Points: non optimized synthesis. Blue points: optimized synthesis by DOE.

3. Conclusion

The benefits of the methodology of the Design Of Experiments for the development of lithium-ion active materials has been highlighted in this work. We strongly believe that it is a powerful tool to save time, experiments and resources but also to obtain “real” optimum of material compositions or synthesis conditions, and not only local ones obtained when only varying each parameter independently.

Bibliography

[1] Murugan, J. Electrochem. Soc., 2009, 156, A79-A83