Development of a Modelling Framework for the Co-Precipitation of NMC Hydroxide as Precursor for Lithium Battery Cathodes

M. Shiea; M.L. Para; G. Tronci; A. Buffo; G. Boccardo; D. Marchisio

Department of Applied Science and Technology, Politecnico di Torino, Turin/Italy

Introduction

The cathode of ubiquitous Lithium batteries is commonly made from $LiCoO_2$, as it is easy to produce and it has high performance and desirable safety characteristics. However, the cost and toxicity of cobalt have been motivating numerous investigations to find alternative materials, particularly by replacing some amount of cobalt with other elements such as nickel and manganese. In this regard, recent studies have shown that $Li(Ni_xMn_yCo_z)O_2$ is a suitable substitute, due to its lower cost, greater safety and comparable performance [1]. This material can be synthesized by calcination of the precursor $Ni_xMn_yCo_z(OH)_2$ (generally called NMC hydroxide) with LiOH. The NMC hydroxide is, in turn, the product of a reactive co-precipitation process initiated by mixing the aqueous solution of metal sulphates with a complexing agent (commonly ammonia) and a basic solution. In the literature, there are experimental investigations, although not many, focusing on the NMC hydroxide co-precipitation, however, little attention has been devoted to the simulation of this process. In this regard, the current work proposes a novel computational framework to simulate the co-precipitation of the NMC hydroxides and characterize precipitated particles. This framework covers the principal aspects of the entire process, i.e. fluid flow, chemical equilibria and particle size evolution, and therefore consists of the following tools: 1) Computational Fluid Dynamics (CFD) to predict the turbulent fluid flow and species transport, 2) a numerically efficient evaluation of the equilibria of the chemical species (using a modified Newton-Raphson method) and 3) the Population Balance Model (PBM) to predict the co-precipitation process and the evolution of the size of precipitated particles. Moreover, the developed framework depends on the models and parameters for the description of the nucleation, breakage and aggregation of particles, which have been identified previously by matching predictions (obtained by a simplified model) with measurements of a micro-mixer reactor (Figure 1). This work focuses on the validation of the entire framework including the models and parameters by performing the CFD-PBM simulation of the micro-mixer and comparing the predictions with the measurements.

Methods

The computational framework is implemented in Ansys Fluent software (v20.2) by employing user-defined functions. The turbulent flow fields in the liquid solution, which govern the transport of the chemical species and solid particles, are predicted by the steady-state pressure-based solver of Ansys Fluent. In addition, the chemical composition of the solution is obtained by solving scalar transport equations for the total concentration of the following species: Ni^{2+}, Mn^{2+}, Co^{2+}, NH_3 and inert ions, i.e. Na^+ and SO_4^{2-}. The total concentrations are used to calculate the chemical equilibria, which includes the reactions for the coordination of the metal cations with ammonia (formation of metal-ammonia complexes), the dissociation of ammonia, and the self-ionization of water [2]. The precipitation reaction is excluded from the equilibria to be able to calculate the supersaturation index, a parameter which is postulated to control the nucleation and growth of particles. The supersaturation is calculated using the equilibrium concentration of the metal cations and hydroxide ion. The framework is completed by coupling the PBM with the CFD model to predict the evolution of particles undergoing nucleation, growth and aggregation. The quadrature method of moments (QMOM) is adopted as the solution method for the PBM. This method tracks the moments of the particle size distribution in the domain by solving the moment transport equations, in which the nucleation, growth and aggregation of particles are described by appropriate models [3]. The transported moments provide information about the integral properties of the particle size distribution, e.g., volume-mean size. Moreover, the moments are used to reconstruct a size distribution that can be compared with the measured distribution.

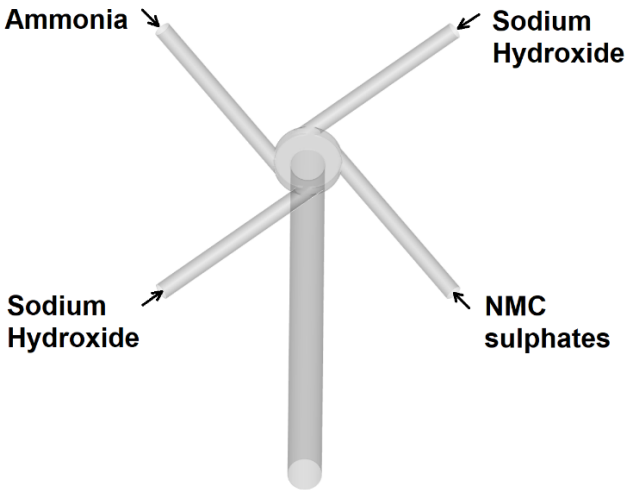

Figure 1: The schematic diagram of the micro-mixer

Results

Figure 2 depicts some predictions obtained by the CFD-PBM simulation of the micro-mixer for a selected experimental case, in which the inlet concentrations of the metal sulphates, ammonia and sodium hydroxide are equal to 0.1 M. In addition, the flow rate of each inlet is set at 17.5 ml/min. As the solutions enter the small mixing chamber of the micro-mixer, they mix very fast and build up the supersaturation, triggering the co-precipitation of the NMC-Hydroxide, i.e., the nucleation and growth of particles. Then, the level of the supersaturation drops as the concentration of the species decreases due to the formation of the solid particles. Figure 2a shows the profile of the supersaturation in the mixing chamber and the top part of the outlet pipe. As mentioned previously, the supersaturation is the key parameter to determine the nucleation and growth rate of particles. In addition, the particles start to aggregate as the number and size of the particles increase as a result of the nucleation and growth processes. These three phenomena determine the properties of the particle size distribution. Figure 2b compares the measured volume-size distribution of the particles with that reconstructed from the predicted moments at the outlet of the micro-mixer. The satisfactory agreement between the measured and predicted particle size demonstrates that the developed framework is a promising approach towards the simulation of pilot- and industrial-scale reactors to produce the NMC hydroxide particles.

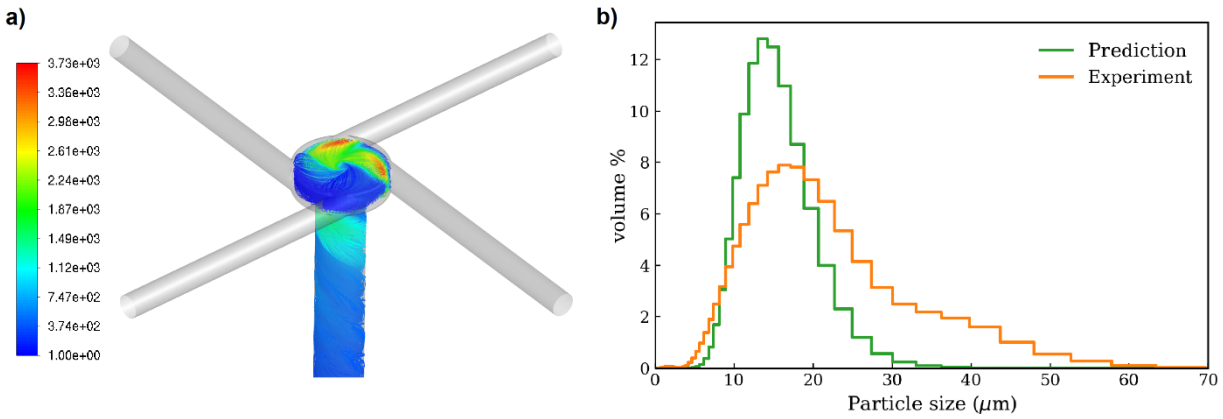

Figure 2: a) The profile of the supersaturation index in the micro-mixer; b) comparison of the predicted and experimental volume-size distribution at the outlet of the micro-mixer

Conclusions

A computational framework was developed to simulate the co-precipitation of NMC hydroxide and predict the characteristics of the formed particles. The framework was used to simulate the precipitation of NMC hydroxide in a micro-mixer and satisfactory

agreement was achieved between the predictions and measurements. In the next stage, the entire model, including the optimized parameters, is used to investigate the performance of scaled-up reactors designed to produce the NMC hydroxide.

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