



# Raman-spectroscopic investigation of sulfate ion concentration change in a continuously stirred tank reactor during the preparation of a cathode material precursor



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## ABSTRACT

The concentration of sulfate ions was continuously monitored by Raman spectroscopy during the preparation of cathode material precursors. The obtained spectra were used for the quantitative analysis of sulfate ions by comparison with a reference solution, and a gradual increase of sulfate ion concentration was detected. Using a mathematical approach, a time-dependent equation describing sulfate ion concentration was theoretically derived, and the calculated concentrations were compared with the measured ones, showing good agreement between these values. Due to the increased sulfate ion concentration, the metal hydroxide cathode precursor became more contaminated with elemental sulfur. Two as-obtained hydroxide powders with different sulfur impurity contents were calcined with a lithium source, producing cathode materials. Electrochemical analysis of the prepared cathode materials showed that morphological aspects (such as particle size) more highly affected the cathode performance more than the sulfur impurity content.

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## 1. Introduction<sup>1</sup>

Lithium-ion batteries (LIBs) have been mostly used for energy storage and conversion devices [1]. Among the high-capacity cathode materials, Ni-rich layered compounds,  $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$  (NCAs,  $x > 0.8$ ), are promising candidates for applications such as hybrid electric vehicles (HEVs), plug-in HEVs, and electric vehicles (EV). Generally, NCAs can be prepared from the high temperature calcination between its hydroxide precursor and lithium sources. Here, NCA hydroxide precursors have been commercially prepared by co-precipitation in a continuously stirred tank reactor (CSTR) [2]. In this method, metal (Ni and Co) sulfates are used as main precursors because of their low cost, causing possible accumulation of sulfate ions within the CSTR system and the inevitable

contamination of NCA hydroxides by sulfur. However, no systematic investigation of sulfate ion concentration change has been conducted to date. It is well known that sulfur impurities should be avoided, since sulfur in the electrode can dissolve in the electrolyte and cause a low open circuit voltage in practical cells through leak current between the anode and the cathode via a shuttle mechanism, which has been considered as a demerit of lithium-sulfur batteries [3,4]. In other literatures, the importance of sulfur impurity control has been discussed [5]. However, the relationship between the concentration of sulfate ions in the CSTR solution and the residual sulfur impurities in NCA hydroxides has rarely been investigated. Typically, the concentration of sulfate ions has been measured using ion chromatography or titration techniques; however, these conventional techniques are difficult to employ in continuous production of hydroxide precursor production using CSTR [6]. Hence, a simple and easy measurement of sulfate ion concentration in CSTR can be highly helpful to investigate the effect of the latter on sulfur impurities in the resulting hydroxide and on the cathode sulfur impurity control. When compared with conventional sulfate analysis methods, Raman spectroscopy is highly suitable, since it is based on laser scattering of the CSTR solution without sampling if optical access to the reactor solution through a transparent window is granted.

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<sup>1</sup> Lithium-ion battery, LIB; Ni-rich layered compound, NCA; hybrid electric vehicle, HEV; electric vehicle, EV; continuously stirred tank reactor, CSTR; scanning electron microscopy, SEM; particle size distribution, PSD; inductively coupled plasma atomic emission spectroscopy, ICP-AES; polyvinylidene fluoride, PVDF; N-methylpyrrolidone, NMP; ethylene carbonate, EC; ethyl methyl carbonate, EMC; galvanostatic charge-discharge measurements, CC-CV

Herein, the sulfate ion concentration in the CSTR was continuously measured using Raman spectroscopy as a function of reaction time. Co-precipitation was conducted using a 4-L CSTR continuously for three days, with overflow solutions continuously analyzed using Raman spectroscopy. Raman spectra of standard solutions with pre-determined sulfate concentrations were used to construct calibration curves, which were used for the quantitative analysis of CSTR solutions. Using simple mass balance between the CSTR input and output rates, a theoretical equation describing the change of sulfate ion concentration was obtained, based on the metal feeding and overflow rates. Based on the latter equation, changes in the measured sulfate ion concentration were compared with the values obtained from Raman spectra. To prepare the NCA cathode, the precursor was calcined with LiOH under O<sub>2</sub> atmosphere at a high temperature ( $\geq 700^\circ\text{C}$ ), and its electrochemical performance was evaluated by coin-type cell measurements.

## 2. Materials and methods

### 2.1. Preparation of precursor and cathode materials

As seen in Fig. 1, the metal sulfate (Ni, Co) and Al solutions were simultaneously fed into the CSTR for 3 days. The average retention time ( $T_R$ ) of the NCA precursor in the CSTR was about 20 h. The NCA hydroxide solution acquired from CSTR overflow was washed, filtered with DI water, and dried in an oven for one day at  $120^\circ\text{C}$ . The obtained NCA hydroxide was calcined with LiOH (Li/M molar ratio = 1.05) under O<sub>2</sub> atmosphere at  $730^\circ\text{C}$  for 12 h in a tube furnace, furnishing the LiNi<sub>0.86</sub>Co<sub>0.12</sub>Al<sub>0.02</sub>O<sub>2</sub> cathode material.

### 2.2. Characterization techniques

X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (PANalytical Emprean) equipped with a rotating anode and utilizing Cu K $\alpha$  radiation ( $\lambda = 0.15406\text{ nm}$ ). The external morphology of the prepared cathode was studied by scanning electron microscopy (SEM, JEOL), while the particle size distribution (PSD) of the NCA precursor was determined using a particle size analyzer (Microtrac s3500). The content of sulfur in the powder was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

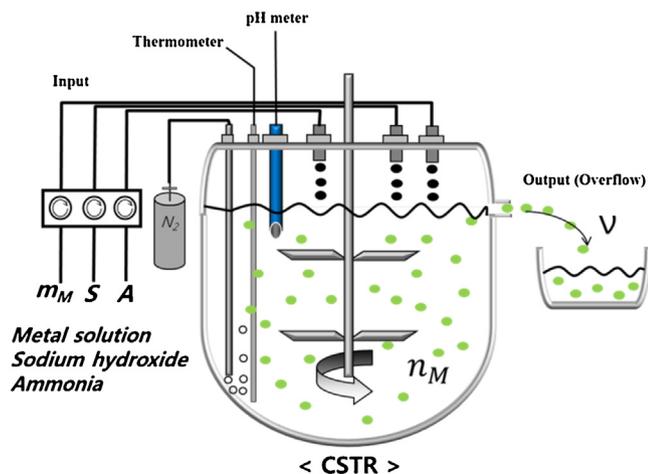


Fig. 1. Scheme of the co-precipitation method used in the CSTR (continuously stirred tank reactor).

### 2.3. Raman measurements

The Raman spectra of solutions were recorded at 84 mW of laser power using an RXPERAM 200 spectrometer (Nanobase, Inc.) equipped with a visible 532-nm laser ( $F = 50\text{ mm}$  achromatic lens).

### 2.4. Fabrication of coin cells

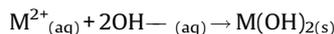
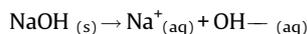
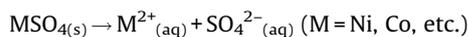
To prepare the cathodes, the obtained NCA powders were mixed with a conducting agent (Denka black) and polyvinylidene fluoride (PVDF) binder in a 94:3:3 ratio (wt.%). The electrodes were prepared by tape casting an *N*-methylpyrrolidone (NMP) slurry of the above mixture on Al foil, followed by pressing and drying at  $120^\circ\text{C}$  for one day. The obtained electrodes were cut into circular pieces with an area density of about 6.9 and  $9.6\text{ mg cm}^{-2}$ . The half-cell parameters were measured with a 2032 coin type cell using 1.0M LiPF<sub>6</sub> in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1:2 v/v) as an electrolyte.

### 2.5. Cathode performance

To examine the cathode performance in lithium-ion batteries, galvanostatic charge-discharge measurements (CC-CV) in a voltage range of 3.0 to 4.3 V vs. Li/Li<sup>+</sup> were conducted. In the rate capability test, the current density was varied from 0.1 to 4C. The cycling performance was recorded at a 1-C discharge rate up to 100 cycles. All electrochemical measurements were conducted using a WBCS-3000 battery cyler (WonA Tech Co.).

## 3. Results and discussion

Fig. 1 schematically shows the co-precipitation reaction in the CSTR [7]. To prepare the hydroxide precursor, the metal sulfate solution (MSO<sub>4</sub>), NaOH (*N*) and ammonia (*A*) solutions were provided as feed solutions, producing the co-precipitated metal hydroxide in the CSTR. During this process, sulfate (SO<sub>4</sub><sup>2-</sup>) and sodium (Na<sup>+</sup>) ions remain unreacted. When all reactants and products are considered, the co-precipitation can be described as follows:



From the above reactions, metal cations and OH<sup>-</sup> ions are continuously consumed to produce the precipitate. In contrast, Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> can be accumulated during the initial period until the steady state is reached.

Fig. 2(a) shows conventional Raman spectra of the supernatant solution from the CSTR overflow after precipitation of NCA hydroxide particles. As can be seen, the Raman shifts between 400 and  $1500\text{ cm}^{-1}$  are due to the various Raman absorptions of the sulfate ions. Here, the  $\nu_1$  peak at  $980\text{ cm}^{-1}$  is assigned to the symmetric stretching mode of the sulfate ion [8–12]. Additionally, the  $\nu_2$  ( $447\text{ cm}^{-1}$ ) and  $\nu_4$  ( $617\text{ cm}^{-1}$ ) modes correspond to the bending vibration and  $\nu_3$  ( $1100\text{ cm}^{-1}$ ) is due to the anti-symmetric stretching mode of the sulfate ion [13]. It is clear that the Raman intensity of the  $\nu_1$  mode was obviously increased by the reaction time increase from 2 to 72 h of CSTR operation, implying an increase of sulfate ion concentration with reaction time, which was reasonable to expect. Regarding the characteristic OH vibrations of water originating from the feed solution, the bending mode (about

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