



# Improving salt-to-solvent ratio to enable high-voltage electrolyte stability for advanced Li-ion batteries

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## ABSTRACT

High-voltage stability of LiBF<sub>4</sub> - propylene carbonate solutions in intermediate concentration range is studied by means of cyclic voltammetry, galvanostatic cycling and X-ray photoelectron spectroscopy using LiCoPO<sub>4</sub> and LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode materials. Coulombic efficiency improves with increasing salt-to-solvent molar ratio from 1:12 to 1:4 (~0.8 m–2.5 m solutions), reaching 98% at 1C charge/discharge rate for 1:4 electrolyte upon cycling of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> up to 5 V vs. Li/Li<sup>+</sup>. The same positive trend is observed for discharge capacities, cycling stability and capacity scattering for both high-voltage cathode materials. X-ray photoelectron spectroscopy of the electrodes studied after cycling in solutions of different concentrations does not reveal any drastic difference in surface composition. Interface pre-formation experiment shows that the presence of the interface layer formed at semi-concentrated 1:4 electrolyte does not have a major impact on the electrochemical properties of the dilute solution. We assume that the enhanced oxidation stability of the concentrated solutions itself is a reason of improving the electrochemical performance rather than the cathode-electrolyte interface properties.

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## 1. Introduction

Since the early history of Li-ion battery development, liquid electrolyte used for commercial cells is typically 1 M solution of LiPF<sub>6</sub> in a mixture of linear and cyclic carbonates such as ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) [1]. This salt concentration provides maximum ionic conductivity in a number of salt-solvent systems [2]. However, due to necessity of further development of the Li-ion technology, other electrolyte properties such as reductive, oxidative and thermal stability are coming to the fore. Electrolytes with increased salt concentration are expected to meet these requirements better than the dilute solutions [3], [4].

An interest to the high-concentrated – or superconcentrated – electrolytes was grown rapidly during last several years. A number of unique properties of such systems were reported: stable Li metal cycling, stable graphite cycling without ethylene carbonate

additive, enhanced interfacial Li<sup>+</sup> transport, low volatility and flammability etc. [3–13]. It is believed that increasing ionic association degree and decreasing the amount of free solvent molecules are the major factors affecting electrochemical properties of high-concentrated solutions. Recently, several papers devoted to high-voltage oxidative stability of the concentrated electrolytes were published. Wang et al. reported on a stable cycling of 5 V-class cathode material (LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> on Al substrate) in Li(SO<sub>2</sub>F)<sub>2</sub>/dimethyl carbonate (LiFSA/DMC) solution at almost 1:1 M ratio [14]. Authors claimed that the proposed electrolyte solution provides low degradation rate during cycling, suppresses Al corrosion and enhances safety of the battery. Doi et al. investigated high-voltage stability of concentrated propylene carbonate (PC) - based electrolytes operating with more conventional salts – LiPF<sub>6</sub> and LiBF<sub>4</sub> [15,16]. For both salts increasing concentration (LiPF<sub>6</sub>:PC molar ratios of 1:12, 1:3.0 and 1:2.2, and LiBF<sub>4</sub>:PC molar ratios of 1:12, 1:2.00, and 1:1.35) suppresses oxidative processes at high voltage and, consequently, increases Coulombic efficiency. However, the overall charge and discharge capacity of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> electrodes decreased with increasing salt concentration until standard acetylene black carbon was replaced with graphitized Ketjenblack. Authors referred this phenomenon to high viscosity of

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the concentrated solution which impedes perfect wetting of the electrode.

Comparing  $\text{LiPF}_6$ - and  $\text{LiBF}_4$ -based electrolytes from practical point of view, the latter seems to be more preferable as it provides better passivation of the Al current collector, better thermal stability and lower moisture sensitivity [17]. The aim of the present study was to explore the “medium-concentrated” range of  $\text{LiBF}_4$ -PC solutions, where compromise between oxidative stability, Coulombic efficiency, on one hand, and viscosity, and cost of the electrolyte, on the other hand, can be achieved. In this contribution we also tried to clarify if the high-voltage stability of the concentrated electrolyte is provided by the electrochemical properties of the solution itself or by a cathode-electrolyte interface usually formed at the electrode surface during cycling [4,18,19].

## 2. Experimental

### 2.1. Materials synthesis and characterization

$\text{LiCoPO}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode materials were prepared using solvothermal synthesis under conditions similar to those described previously [20,21]. To prepare  $\text{LiCoPO}_4$ ,  $\text{H}_3\text{PO}_4$  was drop-by-drop added to concentrated water solution of  $\text{LiOH}$  to form white suspension with a neutral pH ( $\approx 7$ ). After that  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  was introduced into the reaction media. Finally, ethylene glycol (EG) was added (EG:H<sub>2</sub>O = 1:1 vol ratio), and the reactor was sealed and heated to 200 °C under constant magnetic stirring. After conditioning at this temperature during 1 h, the autoclave was cooled, and the precipitate was washed several times by centrifugation. To form conductive coating,  $\text{LiCoPO}_4$  sample was mixed with glucose and annealed at 600 °C for 10 h under Ar atmosphere. For the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  synthesis,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  were dissolved in water in molar ratio of 1:3. Sodium carbonate solution was added and the obtained suspension was heated to 140 °C and conditioned at this temperature for 12 h. The carbonate precipitate was washed, dried and mixed with  $\text{LiOH}$  taken with 5% excess. The precursor was annealed at 350 °C for 2 h and at 800 °C for 10 h with intermediate grinding.

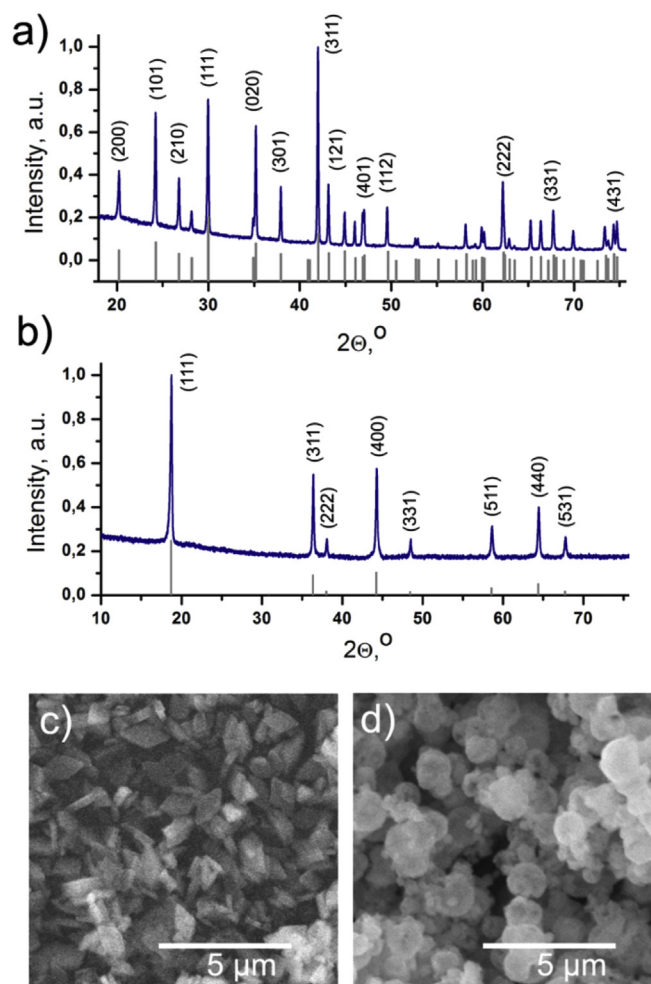
The phase composition of the obtained samples was characterized using powder X-ray diffraction (PXRD, Huber Guinier camera G670,  $\text{CuK}_{\alpha 1}$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ). The observation of particles size and morphology was carried out using a JEOL JSM-6490LV scanning electron microscope (30 kV, W-cathode).

### 2.2. Electrochemical studies and surface characterization

Li-ion electrolyte solutions were prepared by dissolving appropriate amount of  $\text{LiBF}_4$  in PC. We used three concentrations of  $\text{LiBF}_4$  in PC solutions: 0.83, 1.66 and 2.49 mol  $\text{kg}^{-1}$ , which correspond to  $\text{LiBF}_4$ :PC molar ratio of 1:12, 1:6 and 1:4, respectively.  $\text{LiCoPO}_4$ - and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ -based electrodes were prepared by mixing 75 mass.% of the active compound, 12.5% of carbon black (Timcal Super C 65) and 12.5% of polyvinylidene fluoride (PVDF, Solvay Solef 5130) binder in N-methylpyrrolidone and spreading it on an aluminum foil by doctor blade technique. Idle electrodes contained 70 mass.% of carbon black and 30 mass.% of PVDF without any other active material. Dried electrodes were rolled, punched to round discs and dried at 110 °C for 3 h under dynamic vacuum. Two-electrode coin-type cells were assembled in argon-filled glove box (MBraun). Lithium metal was used as the counter electrode. Cyclic voltammetry (2.5–5.3 V vs.  $\text{Li/Li}^+$ , 50  $\text{mV s}^{-1}$ ) and galvanostatic cycling (2.8–4.9 V vs.  $\text{Li/Li}^+$ , C/10–1C rate) were carried out using Elins P-20X8 potentiostat-galvanostat (ES8 software).

For the X-ray photoelectron spectroscopy (XPS) measurements the electrodes after the final charge were removed from the cell in a

glove box and washed with PC by soaking in the solvent for ca. 3 min to remove the adsorbed  $\text{LiBF}_4$ . The electrodes were loaded to spectrometer without contact to atmosphere using the Aldrich AtmosBag attached to the load lock. The as-prepared  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes, carbon black and PVDF were also investigated as reference samples. The surface of the 2.5 m sample was slightly etched with Ar ion beam (0.5 kV, 7  $\mu\text{A}$ ,  $\sim 52^\circ$ ,  $1 \times 1 \text{ mm}$ , Zalar Rotation™) to remove the remained salt residues. XPS measurements were carried out using a PHI VersaProbe II spectrometer equipped with a monochromatic Al  $K_{\alpha}$  X-ray source ( $h\nu = 1486.7 \text{ eV}$ ). XP-spectra for Mn 3p, Li 1s, Ni 3p, S 2p, B 1s, C 1s, N 1s, O 1s, Ni 2p, Mn 2p, F 1s were acquired with analyzer pass energy of 23.5 eV. Such parameters give an opportunity to achieve energy resolution not worse than 0.5 eV with sufficient signal to noise ratio. The particular spectra of the mentioned core levels were approximated with Gaussian-Lorentsian convolution function and Shirley-Tougaard background shape using the Unifit 2014 and MultiPak 9.5 Software. Quantification of composition was performed taking into account analyzer transmission function and core-level and Auger lines overlapping, such as F KLL and Ni 2p, Mn 3p and Li 1s, Mn 2p and Ni MNN.



**Fig. 1.** X-ray powder diffraction patterns and SEM images of  $\text{LiCoPO}_4$  (a,c) and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (b,d) samples. Miller indices are given for the main peaks. Reflections taken from ICDD PDF (#85-0002 and #80-2162 for  $\text{LiCoPO}_4$  and  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , respectively) are shown at the bottom of the patterns.

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