

# Influence of the PVdF binder on the stability of LiCoO<sub>2</sub> electrodes

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## Abstract

We report herein on the effect of the PVdF binder on the stability of composite LiCoO<sub>2</sub> electrodes at elevated temperatures in 1 M LiPF<sub>6</sub> EC/EMC solutions at open circuit conditions. The structure and morphology of composite LiCoO<sub>2</sub> electrodes with different combinations of electrode components (LiCoO<sub>2</sub> active material, PVdF binder, carbon black and current collector) were evaluated by Raman spectroscopy, X-ray diffraction and SEM. The content of Co ions in the electrolyte solutions was determined by ICP. A new effect was discovered, namely, a detrimental impact of the contact between PVdF and LiCoO<sub>2</sub> on the stability of the active mass. The formation of surface Co<sub>3</sub>O<sub>4</sub> and dissolution of Co ions at elevated temperatures is accelerated at the contact points between the active mass and the binder. The effect of water content in the electrolyte solutions on the stability of LiCoO<sub>2</sub> was also studied. The presence of water (and/or HF) is a necessary condition for the accelerated dissolution of Co ions from the active mass. LiCoO<sub>2</sub> oxidizes the solvents at elevated temperatures thus forming CO<sub>2</sub>.

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## 1. Introduction

LiCoO<sub>2</sub> is the main cathode material in practical Li ion batteries [1]. While LiCoO<sub>2</sub> is relatively stable in most of the commonly used electrolyte solutions for Li ion batteries, capacity fading of LiCoO<sub>2</sub> cathodes is always observed upon prolonged cycling and during storage, especially at elevated temperatures [2–4]. Due to the critical importance of the stability of the Li<sub>x</sub>CoO<sub>2</sub> material in its various possible states of charge ( $0 < X < 1$ ) to the performance of commercial Li ion batteries, the capacity fading of these electrodes was intensively studied during recent years.

Among the interesting findings were the phenomenon of Co ion dissolution [4–7], the formation of different inactive surface compounds (Co<sub>3</sub>O<sub>4</sub>, Co<sub>2</sub>O<sub>3</sub> [6] and Li<sub>x</sub>CoO<sub>2</sub> in spinel structure [8,9]), the increase in the electrodes' impedance and the slow down in their kinetics due to the formation of various types of surface films [3,4,10,11]. Co

ions dissolved from the cathode, diffuse/migrate to the anode side, are reduced and form metallic cobalt and cobalt compounds, whose effect on the passivation of the negative electrode is detrimental. It should be noted, that despite the above intensive studies, we are far from understanding all the possible capacity fading mechanisms of this highly important electrode material, and the proper ways to control them. Li ion batteries may be exposed to many critical situations such as high rates, overcharge, overdischarge, elevated temperatures, prolonged storage and different cycling protocols, and thus there may be many different possible routes of degradation and capacity fading for LiCoO<sub>2</sub> electrodes, depending on their exposure to different extreme conditions.

LiCoO<sub>2</sub> electrodes always have a composite structure and composition. In addition to the powdery active mass and the current collector, they have to comprise, conductive additives (usually different types of carbon powder, 2–10%) and a polymeric binder that maintains the integrity of the composite electrodes.

We report herein on an important phenomenon, namely, the detrimental effect of the commonly used binder

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– PVdF, on the stability of composite LiCoO<sub>2</sub> electrodes at elevated temperatures, even when fully lithiated, at open circuit conditions. The electrolyte system in the present study included the commonly used solvents, ethylene carbonate (EC), ethyl-methyl carbonate (EMC), and LiPF<sub>6</sub>, which is the only Li salt that was found suitable so far for commercial applications. The impact of water content in the electrolyte solution was also explored.

The behavior of these electrodes was explored at 60 °C, an elevated temperature easily reached by practical batteries on hot days, especially when the devices that they power are directly exposed to the sun. Hence, the capacity fading mechanism described and discussed in this paper is an important factor that limits the performance of practical Li-ion cells.

## 2. Experimental

LiCoO<sub>2</sub> and CB Powder Super P from LG Corp. and PVdF from Aldrich were used in the fabrication of the electrodes. Ethylene carbonate (EC) and ethyl-methyl carbonate (EMC) Li battery grade were obtained from Merck KGaA (Selectipur<sup>®</sup> series). 1 M LiPF<sub>6</sub> in EC/EMC 1:2 was obtained from Tomiyama (100 ppm HF and 20 ppm H<sub>2</sub>O). The surface area of LiCoO<sub>2</sub> powder (0.4 m<sup>2</sup>/g) was calculated using the BET equation from the adsorption isotherm data, determined by N<sub>2</sub> gas adsorption at 77 K using Autosorb-1-MP apparatus (Quantachrome Corporation). LiCoO<sub>2</sub> electrodes were prepared by two different methods depending on whether they contained a PVdF binder. Those containing a PVdF binder were fabricated by spreading a slurry on aluminum or gold foils, as described elsewhere [12]. PVdF-free electrodes were prepared by pressing LiCoO<sub>2</sub> powder with/without the addition of CB on the Al foil using a hydraulic press (1000 kg/cm<sup>2</sup>).

The structure of electrodes was determined by X-ray diffraction (XRD). XRD patterns were recorded with a BRUKER-AXS, D8-Advance diffractometer using Cu K $\alpha$  radiation. The Co content in the electrolyte solutions was determined with an inductively coupled plasma (ICP) spectrometer (Ultima 2, Jobin Yvon Horiba). Raman spectra were measured ex situ in a back-scattered configuration through the optical glass in hermetically closed cells, using a micro-Raman spectrometer HR800 (Jobin Yvon Horiba), holographic grating 1800 grooves/mm, with an He–Ne laser (excitation line 632.8 nm, 0.9 mW), objective 50 $\times$  (numerical aperture 0.75). Each spectrum presented in this work has an average of at least 3 scans of 1 min each. The morphology of the electrodes was examined by a SEM (JEOL-JSM 840 microscope). FTIR measurements of PVdF samples were carried out using a Nicolet Model 860 FTIR spectrometer in external reflectance mode at a grazing angle. For these measurements, PVdF was extracted from electrodes with *N*-methyl pyrrolidone, applied on a gold mirror and dried in vacuum. UV–Vis spectroscopy of solutions containing Co ions was measured using CARY 1E UV/Vis spectrophotometer, Varian.

LiCoO<sub>2</sub> in the form of powder or in composite electrodes was stored in solutions, hermetically sealed in polyethylene vials under argon in a glove-box atmosphere (<1 ppm O<sub>2</sub>, <2 ppm H<sub>2</sub>O). The vials were thermostated at 60 °C for different periods. All the solutions for the LiCoO<sub>2</sub> soakage were used in the amount of 1 ml per 10 mg of LiCoO<sub>2</sub>.

Three solution compositions for the storage experiments were used:

- (i) EC/EMC (1:2 by volume), 10 ppm H<sub>2</sub>O
- (ii) 1 M LiPF<sub>6</sub> in EC/EMC 1:2, 20 ppm H<sub>2</sub>O, 100 ppm HF
- (iii) 1 M LiPF<sub>6</sub> in EC/EMC 1:2 containing 800 ppm H<sub>2</sub>O.

After two weeks of storage at 60 °C, the solutions were analyzed for Co content by the ICP. The LiCoO<sub>2</sub> powders or electrodes were washed with dimethyl carbonate (DMC), dried in vacuum, and measured by Raman, XRD and SEM.

Electrochemical measurements of LiCoO<sub>2</sub> electrodes were carried out in coin-type cells (2032, standard products from NRC, Canada), and in flooded cells with Li counter and reference electrodes. We used Autolab Systems from Eco Chemie (Netherlands) for voltammetric studies, and Maccor, Inc. model 2000, multichannel battery tester for galvanostatic cycling.

## 3. Results and discussion

Fig. 1 presents two levels of performance of LiCoO<sub>2</sub> electrodes. At a high ratio between the active mass and the solution volume, LiCoO<sub>2</sub> electrodes can be cycled in LiPF<sub>6</sub> solutions even at elevated temperatures (e.g., 60 °C), showing a reasonable stability (Fig. 1(a), capacity fading of less than 0.3% per cycle). However, at a low ratio between the active mass and the solution volume, the capacity fading of LiCoO<sub>2</sub> electrodes in LiPF<sub>6</sub> solutions may be fast even at ambient temperatures, as demonstrated in Fig. 1(b). Some key factors that influence the capacity fading of LiCoO<sub>2</sub> electrodes at elevated temperatures were further rigorously explored.

In several parallel experiments, it was found that LiCoO<sub>2</sub> in composite electrodes is more reactive than LiCoO<sub>2</sub> powder stored in the same solutions/temperatures/periods. For instance, the Raman spectra of aged composite LiCoO<sub>2</sub> composite electrodes clearly show a weak band at 690 cm<sup>-1</sup>, related to the A<sub>1g</sub> vibrational mode of Co<sub>3</sub>O<sub>4</sub> [13], while such a band is not observed with LiCoO<sub>2</sub> powders stored under the same conditions.

To understand which of the components of the composite electrodes accelerates the structural degradation of LiCoO<sub>2</sub>, we prepared four types of electrodes with different combinations of components: LiCoO<sub>2</sub> powder pressed on the aluminium foil; LiCoO<sub>2</sub> powder with the addition of 2.5% CB pressed on the aluminium foil; LiCoO<sub>2</sub> with 2.5% of PVdF on the aluminium foil, and electrodes comprising LiCoO<sub>2</sub>

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