

Copper Coated LiCoO₂ Particles For Water Friendly Electrodes In Li-Ion Batteries

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Metal oxide-based coatings have been applied on LiCoO₂ particles in order to allow the use of water as solvent in the manufacturing process of the cathodes for Li-ion batteries. The coating has been obtained by oxidation of a metallic layer deposited on the particles with electroless deposition. The treatment allowed the deposition of a copper (II) oxide layer on the particles as shown by XPS analysis. SEM investigation demonstrates that particles morphology is unchanged after the plating process. The treatment does not affect the electrodes manufactured with the coated powders of active material show an increased resistance to chemical decomposition in aqueous environment, as shown by electrochemical performances assessment, evaluated by means of galvanostatic cycling in coin cells. Capacity vs. cycles charts show that the stability of the cycling capacity is improved with respect to a cathode made of uncoated LiCoO₂ particles and PVDF latex as binder.

Introduction

Lithium cobalt oxide (LiCoO₂) is the most widespread used active material in conventional cathodes for lithium-ion batteries. Its structural and electrochemical properties have been extensively studied (1-3). The value of LiCoO₂ charge capacity, 150 mA h g⁻¹, is one of the reasons that prompted research in seeking for alternatives to be used as positive electrode material. Plenty of cathode materials have been studied, for example spinels (2,4) and LiFePO₄ (2,5) amongst the others. Moreover, modification of lithium cobalt oxide properties has been achieved by coatings of the active material with different materials and with various techniques (6,7).

Electrodes for lithium ion batteries are produced by mixing the active material and additives with a polymeric binder in an organic solvent, and then casting the produced slurry onto a metallic current collector (aluminum in the case of cathodes). The solvent is then removed from the electrode via evaporation by an annealing treatment. The use of an organic solvent is necessary since LiCoO₂ undergoes chemical decomposition in an aqueous environment (8).

The dominant organic solvent used for the manufacturing of the slurry is N-Methyl-2-pyrrolidone (NMP). NMP has been classified by the European Chemicals Agency as a substance of “very high concern” due to its carcinogenic, mutagenic or toxic for reproduction properties. Moreover, the Environmental Protection Agency of the state of California included NMP in the list of “chemicals known to the state to cause cancer or reproductive toxicity”. With Li-ion battery production doubling every three years, and

accelerating, the battery industry is the main growth driver in NMP usage and likely to become the biggest application for NMP by 2018.

To our knowledge, in literature it is not possible to find a study where NMP usage in electrodes preparation is avoided, using PVDF as binder. The goal of the present work is to develop a NMP-free process using a water-based slurry (9), introducing an electroless copper coating on the LiCoO₂ particles. In this preliminary study the feasibility of the copper plating by conventional electroless solution is proven (10) and the electrochemical performance of the innovative cathode in coin cell device is assessed.

Experimental

Particles of Lithium Cobalt Oxide (Umicore) were electrolessly coated with copper. Before plating, the powder has been catalyzed by an acid palladium-based activation bath. The activation process was done in the following way: powders have been immersed in an aqueous solution containing 0.03 g/l of Palladium Chloride and 1mM HCl (37%) for 1 min. The powder was then separated from the aqueous solution by filtration. Subsequently the powders have been immersed in the aqueous plating bath under magnetic stirring (200 rpm). Composition of the deposition bath is as follows: 6 g/l copper sulfate, 7.47 ml/l formaldehyde, 27 g/l ethylenediaminetetraacetic acid, 5.6 g/l sodium hydroxide, from Sigma Aldrich. The plating temperature was 60°C and pH value was 10. After the deposition, the copper coated LiCoO₂ powder was then dried in an oven at 100°C for 2 hours. To prepare the electrodes, an aqueous slurry was casted onto the current collector, made of aluminum. The aqueous slurry was prepared by mixing the following ingredients: active material (coated and non-coated LiCoO₂), deionised water, SuperP (conductive carbon black), carboxylated methyl cellulose (CMC) and PVDF (Solvay). The adhesion of the slurry on the aluminum foil was then enhanced by an annealing treatment, which ensured the complete evaporation of the water from the cathode. Coin cells have been prepared in a glove box (MBRAUN Labmaster 130) under protected atmosphere. A 14 mm disk of the prepared electrode was punched as cathode, while metallic lithium, served as counter electrode. The electrolyte was 1M LiPF₆ in EC/DMC (1:1), a Whatman glass-fiber paper was used as separator. Conductivity measurements and electrochemical measurements have been made using a potentiationstat/galvanostat (BT2000, Arbin Instruments). XPS measurements were carried out with a PHI 5600 ci spectrometer equipped with an Al monochromatic anode and a spherical capacitor analyzer (SCA).

Results and Discussion

LiCoO₂ particles have been coated with an electroless copper layer. The overall reaction involving the metallic ions and the reducing agent is the following:



The copper ions reduction process is autocatalytic, and allows the deposition of a uniform and continuous metallic layer which can be annealed to promote the formation of a copper oxide-based coating, as sketched in Fig. 1.

SEM images show the particles of lithium cobalt oxide before, Figure 2, and after 60 minutes of plating, Figure 3. Moreover, from this analysis it is not noticeable any sign of degradation on particles' surface, after the 2-step metallization process; however, this

point will be addressed in the future work. The images show that the morphology of the particles is unchanged after the permanence for 60 minutes in the plating bath.

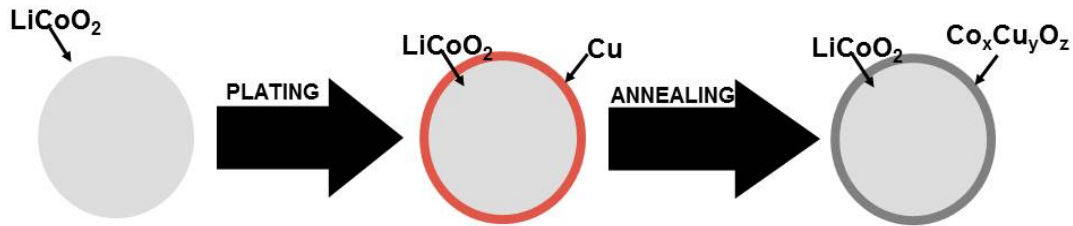


Figure 1. Schematic representation of the coating layer obtained by copper electroless deposition and subsequent oxidation.

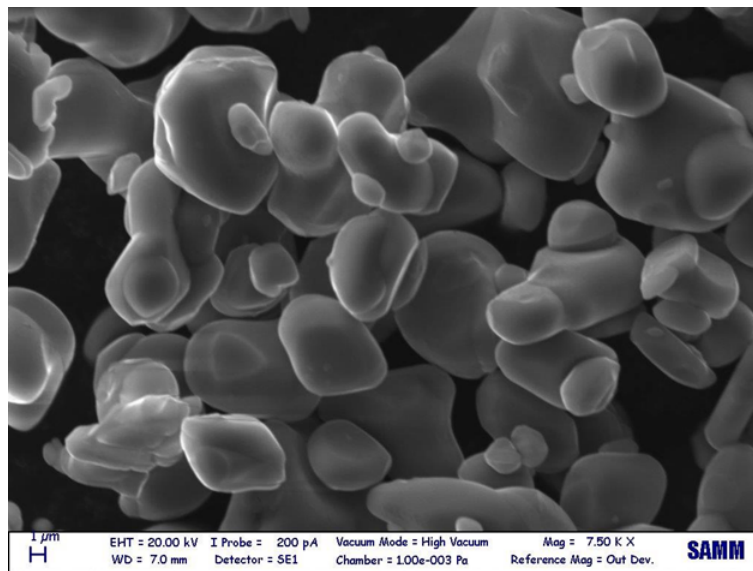


Figure 2. Morphology of uncoated lithium cobalt oxide obtained by SEM analysis.

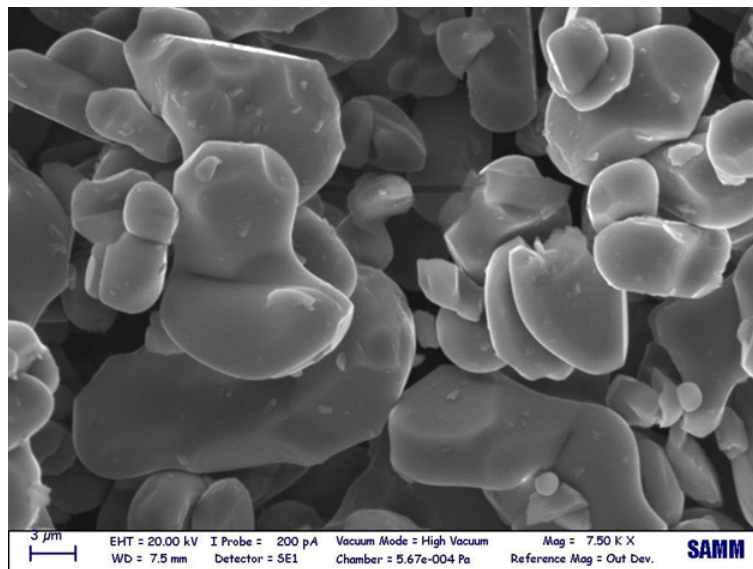


Figure 3. Morphology of coated lithium cobalt oxide obtained by SEM analysis.

The obtained EDX spectra from the coated particles, Figure 4, is showing a weak signal corresponding to the presence of copper in the sample containing coated particles. XPS

measurements have been carried out in order to establish whether the copper is existing in its elemental form or as oxide. The XPS survey measurements confirm the presence of copper with the surface composition presented in Table 1.

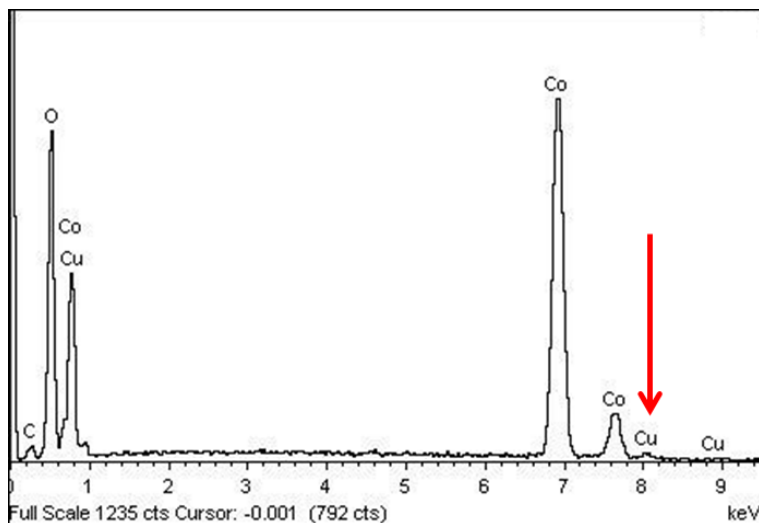


Figure 4. EDX spectra obtained from the uncoated lithium cobalt oxide particles. The arrow is indicating the peak assigned to copper.

Table 1. Surface atomic composition of lithium cobalt oxide particles before and after treatment, obtained by XPS analysis.

	Li	Co	O	Cu
LCO – Before Treatment	9.34 %	45.28 %	44.74 %	-
Cu-LCO – After 60 min Treatment	8.55 %	43.67 %	45.21 %	2.56 %

The high-resolution spectra obtained from the analysis of Cu2p orbital are shown in Figure 5 and 6, for uncoated and coated lithium cobalt oxide particles, respectively. An analysis of the spectra is showing that for the untreated Lithium Cobalt Oxide there is no signal characterizing the presence of copper in the sample, while the treated Lithium Cobalt Oxide is showing four peaks in the range of binding energies typical of copper. Biesinger et al. [11] studied the surface chemical state of various transition metal, and a comparison with their interpretation is confirming the presence of copper on the particles in the form of copper (II) oxide (CuO).

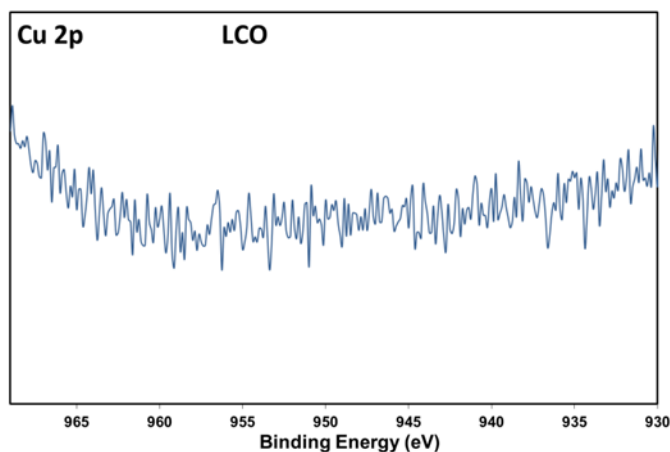


Figure 5. High-resolution XPS spectra of Cu 2p for uncoated lithium cobalt oxide particles.

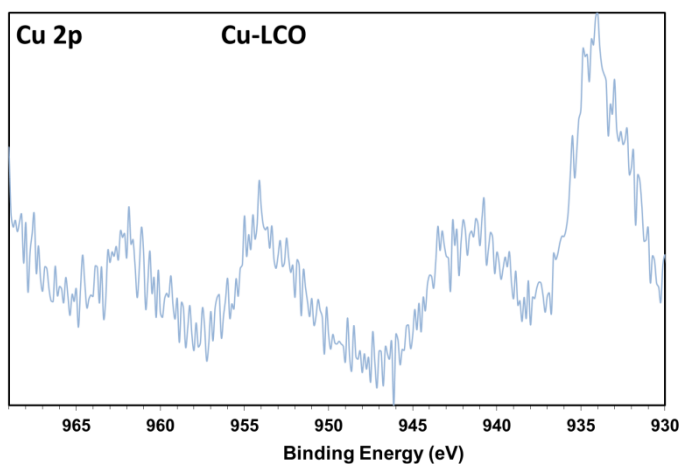


Figure 6. High-resolution XPS spectra of Cu 2p for coated lithium cobalt oxide particles.

The position of the peaks could suggest the presence of copper hydroxides on the surface of the particles, but the formation of hydroxides of any form on the surface of the particles is inhibited by the thermal treatment at which the particles undergo after the metallic coating. In fact, the annealing treatment in air has been designed to achieve three different goals: eliminate residual water from the powders, eliminate all the hydroxides that can be present at the surface of the particles, thus promoting the formation of copper oxides by oxidation of metallic copper obtained with electroless deposition.

The impact on the overall electrochemical performance of an electrode containing coated lithium cobalt oxide has been assessed by means of galvanostatic cycling in a coin cell system. Two samples of cathodes have been prepared using PVDF latex as binder, and bare lithium cobalt oxide and coated lithium oxide as active material, respectively. The anode material was metallic lithium for both batteries. The cells have cycled for 10 cycles at a rate of 1C. Results of this test are displayed in Figure 7.

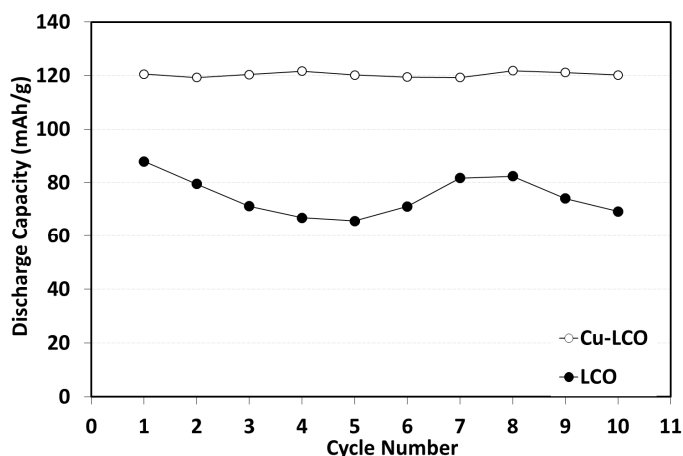


Figure 7. Reversible capacity versus cycles for LCO (black circle), Cu-LCO (white circle) with 10 cycles at 1C.

From the results of the cycling test, it can be noted a marked difference between the two electrodes. LCO is showing a fluctuating behavior, with capacity values well below 100 mAh/g. The instability of the cycling values is due to the progressive degradation of the material occurring during lithiation/delithiation cycles. Moreover, a difference in the value of reversible capacity with respect to the electrode containing coated lithium cobalt oxide, Cu-LCO, is already noticeable at the first cycle. This discrepancy is due to the barrier effect that the coating has on the particles during slurry preparation and electrode casting. Lithium cobalt oxide undergoes chemical decomposition when in contact with water, and this leads to a decrease of capacity values during the life of the battery. The copper oxide coating is capable to counteract to this behavior allowing a more stable cycling behavior with capacity values over 100 mAh/g at 1C. The results have proven to be reproducible after a series of repeated tests (at least 3 for each condition), so it can be excluded that the variation of battery performance is due to variance during battery manufacturing.

Conclusions

Lithium cobalt oxide particles have been coated with a copper oxide-based coating. This has been done using the electroless deposition technique, and consequent annealing in air. The coating process did not alter the morphology of the particles while increased the cycling performances of the obtained electrodes. The chemical composition of the coating was analyzed by XPS analysis which confirmed the presence of copper (II) oxide on the surface of the particles. Thus, water-based slurries can be used during the preparation of the cathode, e.g. using PVDF latex as binder. The electroless deposition is therefore a promising technique to perform a coating on the surface of the particles, and its versatility in the choice of the metallic element to deposit opens new opportunities in the field of active material modification for application in lithium ion batteries.

Acknowledgments

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