

# PVDF Latex As a Binder for Positive Electrodes in Lithium-Ion Batteries

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## 1. INTRODUCTION

Vinylidene fluoride (VDF) polymers are known in the state of the art to be suitable as binders for the manufacture of electrodes for use in nonaqueous-type electrochemical devices such as batteries, preferably secondary batteries,<sup>1</sup> and electric double layer capacitors.<sup>2</sup>

In commercial grade lithium batteries, techniques for manufacturing electrodes involve the use of organic solvents for dissolving VDF polymer binders and homogenizing them with a powdery electrode material and all other suitable components to produce a paste (slurry) to be applied to a metal collector.

The role of the organic solvent is typically to dissolve the VDF polymer in order to bind the powdery electrode material particles to each other and to the metal collector upon evaporation of the organic solvent. The use of an organic solvent is necessary since LiCoO<sub>2</sub> is not stable in an aqueous environment.<sup>3</sup> The dominant organic solvent used for the preparation 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.<sup>4</sup>

Nevertheless, more recently, approaches are pursued wherein the use of organic solvents is avoided so as to ensure more environmentally friendly techniques, and waterborne solutions have been proposed for cathodes manufacturing, for example, using polymeric water emulsions or poly(acrylic acid) as a binder.<sup>5,6</sup> However, an assessment of cycling performances for water-based cathodes with respect to NMP-based cathodes has not been performed yet.

Lithium cobalt oxide (LCO) is the most widespread active material in conventional cathodes for lithium-ion batteries. Its structural and electrochemical properties have been extensively studied.<sup>7–9</sup>

The available value of LCO specific capacity, generally around 150 mA h g<sup>-1</sup>, is one of the reasons that prompted research in seeking for alternatives to be used at the positive electrode. Plenty of cathode materials have been studied, for example, LiMn<sub>2</sub>O<sub>4</sub> spinels<sup>8,10</sup> and LiFePO<sub>4</sub><sup>8,11</sup> among others. Moreover, modification of lithium cobalt oxide properties has been achieved by coating the active material with different materials and with various techniques.<sup>12</sup> In particular, coatings made of metal oxides, like MgO and Al<sub>2</sub>O<sub>3</sub>,<sup>13–15</sup> are able to enhance the electrochemical stability of the LiCoO<sub>2</sub> cathode and thus to improve overall performance of the battery.

The present work is the first step toward the development of an industrial NMP-free process for electrodes manufacturing using a water-based slurry, keeping PVDF as a polymeric binder.<sup>16</sup> The decomposition of the active material particles in an aqueous environment is avoided by coating the particles with copper oxide, obtained by plating using the electroless technique and subsequent annealing of the powders. The feasibility of the copper plating by conventional electroless solution will be assessed using a lab scale plating treatment.<sup>17</sup> Then, the possibility of a scale-up of the coating process is shown with a semi-industrial plating treatment (pilot filter dryer). Characterization of coated active material and obtained electrodes will be carried out to evaluate the presence of the metal-based layer on the particles. Electrochemical performances of the water-based cathodes will be assessed and compared with a NMP-based electrode.

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## 2. EXPERIMENTAL SECTION

### 2.1. LiCoO<sub>2</sub> Powders Preparation on the Lab Scale.

Particles of LiCoO<sub>2</sub> (Umicore Korea, commercial grade) have been coated with metallic copper by electroless plating on a lab scale. Prior to copper deposition, the powder was catalyzed by a wet process of palladium activation. This activation process was carried out by immersion of the powder in an aqueous solution containing 0.03 g/L of palladium chloride (Sigma-Aldrich, commercial grade) for 1 min. Then, the powder was immersed under magnetic stirring (200 rpm) in the aqueous plating bath, which contained 6 g/L of copper sulfate, 7.47 mL/L of formaldehyde, 27 g/L of ethylenediaminetetraacetic acid (EDTA), and 5.6 g/L of sodium hydroxide, all from Sigma-Aldrich and of commercial grade. The plating temperature and pH value of the plating solution were 60 °C and 10, respectively. After the deposition, the copper coated LiCoO<sub>2</sub> powder was then annealed in an oven at 200 °C for 1 h.

### 2.2. LiCoO<sub>2</sub> Powders Preparation at Industrial Scale.

Particles of LiCoO<sub>2</sub> have been coated with metallic copper by electroless plating on a semi-industrial scale using pilot filter dryer model LABO TD-PF 10 from Comber.

The scheme of the reactor is given in Figure 1.



**Figure 1.** Pilot filter dryer model LABO TD-PF 10 from Comber (picture courtesy of Comber).

Using the system shown above, the solutions were loaded from the valve placed in the upper part of the reactor. The filtrations at the end of both coating steps were made possible by the presence of a PTFE filter (porosity 3 μm) placed at the bottom of the vessel.

The compositions and process parameters of the aqueous solutions used in the coating treatment are unvaried with respect to the lab scale process. Nevertheless, the use of the reactor involved some changes in the operative steps of the process. In fact, between the activation bath and the plating bath, it was necessary to rinse the vessel in order to avoid contaminations of the solution containing copper ions and formaldehyde.

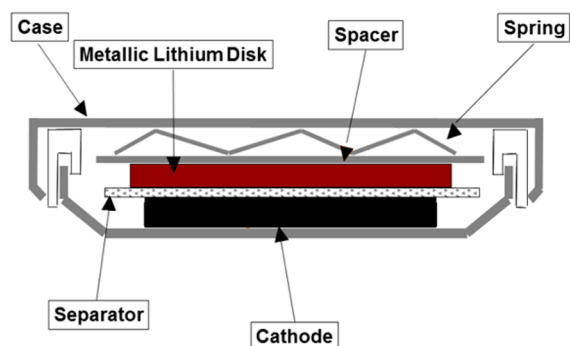
The volume of the vessel allowed the treatment of a quantity of powders up to 500 g for each reaction batch. This quantity was chosen to ensure a good dispersion of the particles during the treatment, thus avoiding excessive agglomeration of particulate.

Commercial solutions used to perform the up-scale of the coating process have been purchased from Atotech GmbH.

### 2.3. Electrode and Coin Cell Preparation.

To prepare the cathodes, it was necessary to cast an aqueous slurry onto an aluminum foil, which served as a metallic current collector. The aqueous slurry was prepared by mixing the prepared LiCoO<sub>2</sub> powders (54% in weight with respect to the weight of the slurry at the end of the mixing step) with SuperP (3%, conductive carbon black, TIMCAL), deionized water (32.3%), carboxylated methyl cellulose (0.3%, Sigma-Aldrich), and an organic binder (PVDF, 10.4%, Solvay). Electrode adhesion on the metallic current collector was improved with an annealing step at 200 °C.

Coin cells have been prepared in a glow box (MBRAUN Labmaster 130) under an Ar gas atmosphere by punching a 14 mm disk of the prepared electrode with metallic lithium, which served as counter and reference electrodes. The electrolyte was 1 M LiPF<sub>6</sub> (Merck) in ethylene carbonate/dimethylcarbonate, and a Whatman glass-fiber paper was used as a separator. The scheme illustrating the stack of materials present in the coin cell tested in this work is depicted in Figure 2.



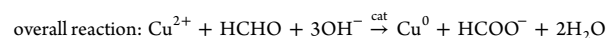
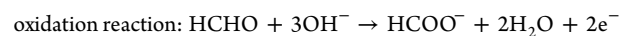
**Figure 2.** Scheme of the coin cells used in the electrochemical testing.

### 2.4. Characterizations.

SEM measurements have been performed using an FE-SEM model Leo Supra 35. Conductivity measurements and electrochemical measurements were performed using a potentiostat/galvanostat (BT2000, Arbin Instruments). In particular, the performances of the cathodes have been tested by galvanostatic cycling of coin cells, with cutoff potentials of 3.2–4.2 V.

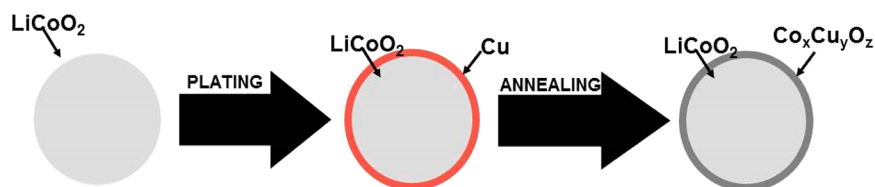
## 3. RESULTS AND DISCUSSION

Copper electroless coating has been applied to LiCoO<sub>2</sub> particles after Pd activation. The complete reaction scheme is the following:

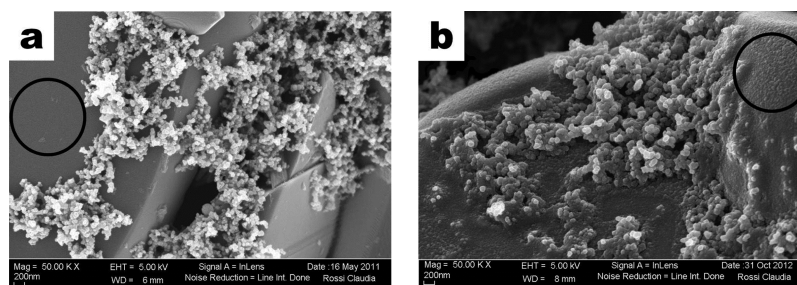


During the deposition process, formaldehyde is oxidized and copper is reduced in proximity of the active sites present at the surface of the particles. The copper ions reduction process is autocatalytic, leading to a uniform and conformal coating of the entire particle. The copper oxide is then obtained by oxidation of the metallic layer during an annealing treatment after the deposition process as sketched in Figure 3 and confirmed by SEM analysis shown in Figure 4.

The process used for applying the coating on the particles does not allow precise control on the chemical composition of the coating. Even though the annealing step (1 h at 200 °C)



**Figure 3.** Schematic representation of the coating layer obtained by copper electroless deposition and subsequent oxidation.



**Figure 4.** SEM images of the cathodes containing uncoated (a) and coated (b)  $\text{LiCoO}_2$  particles. Higher roughness of the treated particles indicates the presence of the copper oxide layer on the active material (compare surfaces in the black circles).

should ensure the formation of a deposit of  $\text{CuO}$  on the surface of the particles, it is not possible at the moment to exclude the formation of a solid solution with cobalt. Further investigations, by XPS analysis for instance, are needed to clarify this point; this is why a generic formula for the composition of the coating ( $\text{Co}_x\text{Cu}_y\text{O}_z$ ) was used in Figure 3.

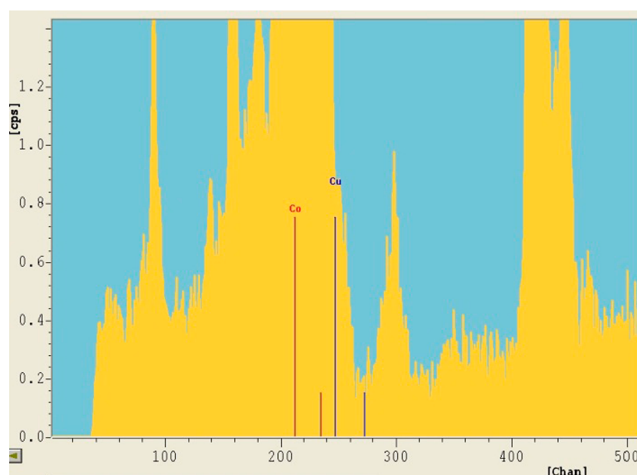
SEM images show the particles with the binder, in the form of a spongy deposit, in contact with them. The surface of the treated particles (Figure 4b) shows an increased roughness level with respect to the untreated (Figure 4a)  $\text{LiCoO}_2$  particles. This modification of the active material surface, indicates the presence of a homogeneous layer.

When particles are incorporated in the electrode, the metallic oxide coating has a 2-fold beneficial effect on the electrochemical performances of the cathode. First, it increases the conductivity; second, it isolates  $\text{LiCoO}_2$  powders from water during electrode preparation, so avoiding degradation, thus increasing the stability of the electrode upon cycling, holding down the capacity fading during lithiation and delithiation processes. Such advantages due to the presence of the copper oxide layer on the particles are strongly affected by the quality of the film. In fact, if the layer is not uniform throughout the surface of the powders, the effectiveness of the coating would be reduced. In particular, the barrier effect would be influenced, resulting in poor performances of the electrode over cycling time due to the breaking up of the active material upon water contact.

XRF analysis has been carried out in order to investigate the presence of copper on the surface of the powders after the electroless plating and annealing. Results are shown in Figure 5.

The analysis reveals the presence of a small quantity of copper in the analyzed sample. In particular, the peak of copper is present as a small shoulder of the broader peak of cobalt. The shape of the peak suggests that only a small quantity of copper is present on the surface of the particles. Further analyses will be carried out to determine the actual nature of the copper-based coating required.

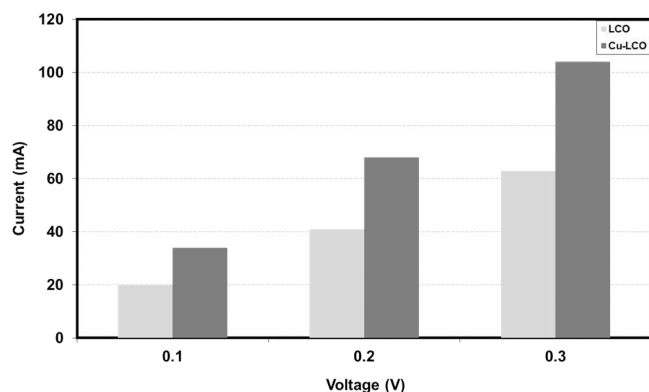
Another test to confirm the presence of copper on the powders regarded electrical conductivity of the prepared electrodes. Measurements have been done on two samples, one containing  $\text{LiCoO}_2$  particles (LCO) and one with copper



**Figure 5.** XRF analysis on LCO powders after the electroless plating and subsequent annealing treatment.

coated particles (Cu-LCO), respectively. Samples have been sandwiched between two electrodes, and a voltage has been applied to the system. The circulating current was then measured. Results are shown in Figure 6.

Circulating current is always higher in the Cu-LCO electrode with respect to the one containing nontreated particles, LCO. Linear fitting of the data allowed the calculation of the resistance offered by the electrodes during the tests, with values 4.81 and 2.9 ohm for LCO and Cu-LCO, respectively, for the whole electrode system, i.e., current collector and active material. Higher circulating current in the Cu-LCO electrode confirms the existence of copper oxide coating on the particles. The presence of an element with higher electric conductivity inside the electrode is enhancing its overall performance. This is because inside the electrode, particles are packed together, and the copper oxide coating is thus forming a network expanded throughout the whole electrode. This network can act as a bridge between particles, building up channels where ions and electrons can preferentially flow when an external stimulus is applied to the system.



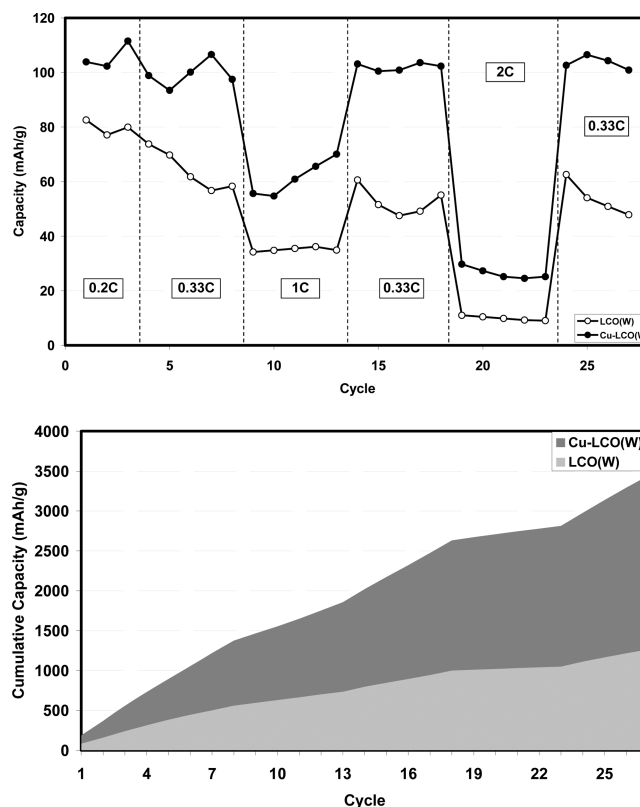
**Figure 6.** Conductivity measurements on cathodes with nontreated (light gray bars) and treated (dark gray bars) powder.

The presence of the copper coating is effectively enhancing the conductivity properties of the electrodes, but no information can be deduced about its influence on the electrochemical performances. In particular, the eventual hindering of the lithium ions' mobility during charge/discharge cycles by the metal oxide layer on the particles is very important, as it would heavily affect the performance of the electrode. Moreover, the structural stability of the active material is a fundamental factor in assessing the performances of the cathode. All these aspects can be guaranteed only if the uniformity of the coating is ensured all over the electrode. This is the main reason that drove the choice on the electroless deposition technique to apply the metallic layer: the possibility of obtaining conformal and uniform films regardless of the geometry of the particles to coat.

To assess the electrochemical performance of the  $\text{LiCoO}_2$  particles coated with copper on a lab scale level, coin cells were prepared and were cycled with the following schedule: three cycles at 0.2C, five cycles at 0.33C, five cycles at 1C, five cycles at 0.33C, five cycles at 2C, and four cycles at 0.33C. This sequence of different cycling rates has been thought to stress the electrodes, in order to assess the reversibility of the lithiation/delithiation sequences occurring during charge/discharge cycles. In this test, two coin cells are compared: the first, LCO(W) contains uncoated LCO; the other, Cu-LCO(W), contains coated LCO. In both cases, water has been used as a solvent for the electrode preparation ("W" stands for water).

Figure 7 shows the results of the cycling behavior of the tested samples, in terms of values of reversible capacity versus cycles and cumulative capacity versus cycles.

The performance of the coin cells denotes a marked difference between the two samples. The cathode containing the treated particles (Cu-LCO(W)) shows higher reversible capacity in all cycling conditions with respect to the cathode with untreated particles (LCO(W)). Moreover, Cu-LCO(W) shows a high reversibility of the lithiation process, being its capacity in the last cycle at the same levels with respect to the beginning of the test ( $>100 \text{ mAh/g}$ ). LCO(W) shows a slight decrease in the performance during cycling, with values reversible capacity around  $50 \text{ mAh/g}$ . This is a clear indication that the contact with water during the electrode preparation has caused some kind of deterioration of the uncoated LCO, whose effects become fully visible during the life of the battery. The progressive degradation of the performance can be highlighted by calculating the capacity retention between the values of



**Figure 7.** Reversible capacity versus cycles and cumulative capacity for the tested cathodes at various cycling rates. Cutoff potentials are 3.2–4.2 V.

reversible capacity of the two electrodes at the first and at the last cycle of this test. The results are shown in Table 1.

**Table 1. Electrochemical Performances for the Coin Cells<sup>a</sup>**

|           | $RC_s$ ( $\text{mAh g}^{-1}$ ) | $RC_e$ ( $\text{mAh g}^{-1}$ ) | capacity retention |
|-----------|--------------------------------|--------------------------------|--------------------|
| LCO(W)    | 82.5                           | 47.8                           | 58%                |
| Cu-LCO(W) | 103.9                          | 100.9                          | 97%                |

<sup>a</sup> $RC_s$ : reversible capacity measured after 1 cycle.  $RC_e$ : reversible capacity measured after 27 cycles. Capacity retention is the ratio between  $RC_e$  and  $RC_s$ .

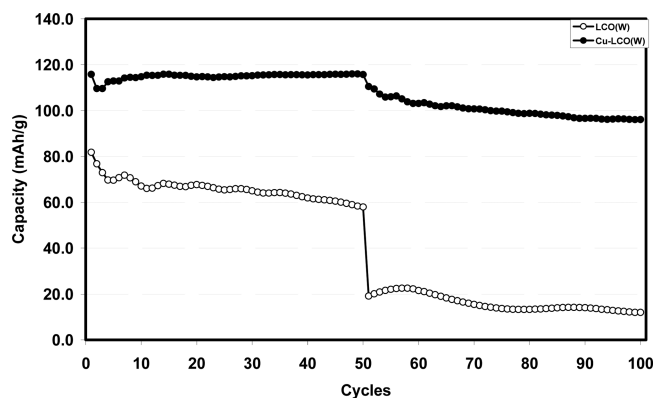
The capacity retention for Cu-LCO(W) has a value of 97%, which denotes a high degree of reversibility in the lithiation phenomena during cycling. The electrode LCO(W) has a capacity retention of 58% with respect to the first cycle, which denotes that the degradation occurred at the cathode during charge/discharge cycling. It seems that LCO(W) progressively deteriorates, causing a continuous worsening of electrical continuity in the electrode, which in turn heavily affects the global capacity of the cathode. From this perspective, capacity retention can be seen as an index of the degree of decomposition of the  $\text{LiCoO}_2$  powders. Even though these results appear a direct consequence of the water-based process used during electrode preparation, it is difficult to explain why the LCO(W) deterioration continues during the battery operation, when water is long since gone. A specific experimental work would be needed to clarify this point.

While an aqueous environment is detrimental for the LCO(W) electrode, it is not for the Cu-LCO(W) cathode. In our opinion, this is because the copper oxide coating applied on



the particles has effectively protected the active material from degradation during the contact with water. To confirm this statement, a comparison with an LCO-based electrode not affected by any water treatment will be provided and discussed in the next sections. Moreover, the good battery performance indicates that the copper oxide coating does not hinder the flow of lithium ions and electrons during charge/discharge cycles. It is worth it to note that also the metallization process implies contact with water, but the contact time is much less than that required for electrode preparation (about 1 min vs at least 1 h). In fact, one of the main causes that leads to a decrease of performances of the battery is cobalt dissolution from the cathode during battery cycling.<sup>18</sup> The water could progressively damage the surface of the particles when the latter are dispersed in aqueous media, catalyzing the dissolution of lithium and cobalt from the powders. This would negatively affect the surface of the active material, promoting irreversible cobalt dissolution phenomena during cycling.

The necessity of the coating treatment as enabling technology for the use of PVDF latex as a binder in cathodes for Li-ion batteries is confirmed by the following test. Cycling performances of the two electrodes have been assessed using a different schedule from the previous test: 50 cycles at 0.33C and 50 cycles at 1C. The goal of this sequence of cycling rates is to evaluate the effect of a stress which lasts for a longer time (higher number of cycles). Results of this test are shown in Figure 8.



**Figure 8.** Reversible capacity versus cycles for the two LCO(W) (open circles) and Cu-LCO(W) (black circles) with 50 cycles at 0.33C and 50 cycles at 1C. Cutoff potentials are 3.2–4.2 V.

This test is showing a marked difference in the cycling behavior of the two electrodes. The reversible capacity level for Cu-LCO(W) shows a slight decrease in the first cycles with respect to the value measured after the first charge/discharge cycle, followed by a progressive recovery during the completion of the first step of the schedule. After 50 cycles, the electrode shows a decrease in performance that is compatible with the increase of the cycling rate to 1C, with reversible capacity forming a plateau just below 100 mAh/g.

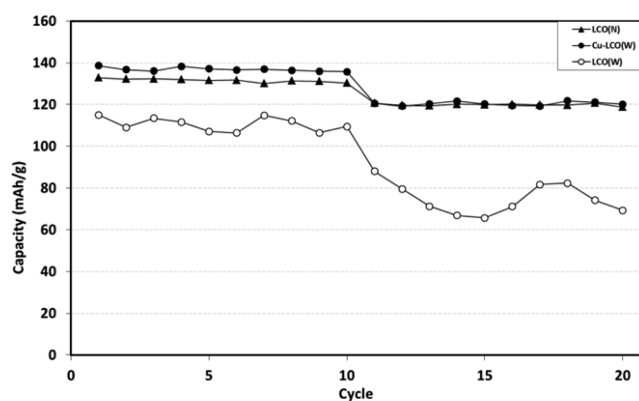
In the first part of the test, the electrode containing noncoated active material, LCO(W), exhibits values of capacity sensibly lower than Cu-LCO(W). After the increase of cycling rate to 1C, the reversible capacity falls to values around 20 mAh/g, highlighting a fluctuating behavior without the presence of a plateau.

The trends characterizing the two tested electrodes are in accordance with the decomposition of the LCO when in

contact with an aqueous environment, a condition that took place during electrode preparation. In particular, Cu-LCO(W) is confirming the results obtained in the test shown in Figure 7 at the same discharge rate (0.33C and 1C), while LCO(W) exhibits specific capacity values sensibly lower than the ones obtained in the first test at the discharge rate of 1C. The performances, and their poor reproducibility, of LCO(W) can be explained with the fact that the active material present in the electrode is not able to ensure lithium intercalation at a level comparable to Cu-LCO(W). In particular, the capacity decay upon cycling for LCO(W) at 1C can be explained if we analyze the cycling schedule used in this test: when the cycling rate is increased to 1C, the battery has already completed 50 cycles at 0.33C, which already degraded the electrode up to a certain extent. After this number of cycles, the cathode cannot offer the same performance level, suggesting that degradation phenomena, caused by prolonged contact with water prior to cycling, become more evident after a long cycling schedule, even at low cycling rate, rather than short cycling schedules. Since the only difference in the manufacturing procedure between the two cathodes is the metallization process, it can be stated that the copper oxide coating plated on the powders of active material is able to counteract the deteriorative action of the aqueous environment on the LCO powders during slurry preparation when using a PVDF latex as a polymeric binder.

Another cycling test has been done in order to perform a comparison of the two electrodes tested so far with a reference cathode, which was prepared following the state-of-the-art process, where the electrode is prepared using the organic solvent *N*-methyl-2-pyrrolidone (NMP) as a liquid medium. The active material contained in this cathode was not coated using the electroless deposition technique. In the following, this sample is labeled “LCO(N)”

Figure 9 shows the results of a cycling test for three samples: LCO(N), LCO(W), and Cu-LCO(W). The schedule used in this test is the following: 10 cycles at 0.33C and 10 cycles at 1C.

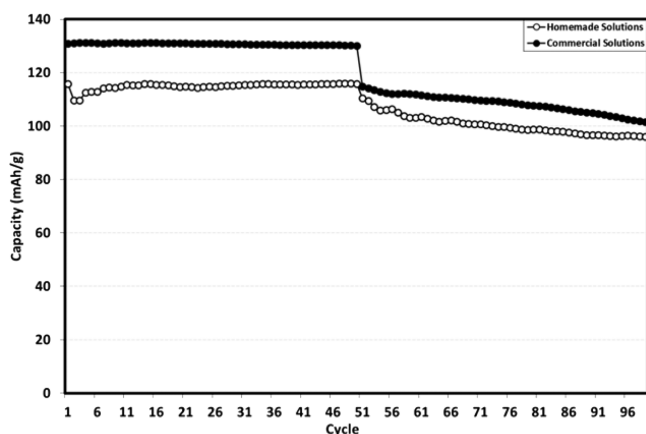


**Figure 9.** Reversible capacity versus cycles for LCO(N) (black triangle), Cu-LCO(W) (black circle), and LCO(W) (open circle) with 10 cycles at 0.33C and 10 cycles at 1C. Cutoff potentials are 3.2–4.2 V.

The results of the cycling test confirm that the use of PVDF latex at the cathode yields performances comparable to NMP-dispersed PVDF. This occurs only when the active material is coated with copper oxide. The behavior of LCO(W) confirms its fluctuating and unstable trend, which was denoted in Figure 8. LCO(N) and Cu-LCO(W) show similar performances at cycling rates of 0.33C and 1C, respectively. The slight

discrepancy in the specific capacity values for Cu-LCO(W) and LCO(W) with respect to data previously shown in Figures 7 and 8 can be attributed to minor setup issues during battery manufacturing, as the electrodes have been prepared using the same protocols with respect to other tests.

In order to explore the feasibility of an upscale to a semi-industrial level of the metallization process, an assessment of the electrochemical performances of the electrode containing LCO powders metallized using a Comber pilot filter dryer has been done. Results are shown for two electrodes containing copper oxide coated powders. Both samples are prepared using PVDF latex as a binder. In the first case, powders have been metallized using commercial solutions from Atotech GmbH, while in the second case, homemade solutions have been used. Coin cells have been cycled for 50 cycles at 0.33 C and 50 cycles at 1C. Figure 10 shows the results obtained from this cycling test.



**Figure 10.** Capacity versus cycles performance for the cathodes prepared with LCO powders metallized using commercial solutions (black circle) and homemade solutions (open circle). Cutoff potentials are 3.2–4.2 V.

From the chart in Figure 10, it can be seen how the use of commercial grade solutions enhances the performance of the electrode manufactured using PVDF latex. In fact, the combination of the commercial solution with the pilot filter dryer positively affects the stability of the cycling behavior of the cathodes.

#### 4. CONCLUSIONS

It was possible to manufacture electrodes using a water based binder, PVDF latex, with cycling performances comparable to a reference electrode (solvent based). The coating process allowed the protection of the active material from the aqueous environment that occurs during the cathode preparation. In this way, it is possible to have a green alternative to the well-established organic solvents that are dominating the Li ion battery market. The coating is effective even though the whole electroless process (palladium-based activation and copper plating) is performed in an aqueous environment. This is just an apparent contradiction, since when LCO powders are dispersed in the  $\text{CuSO}_4$ -based plating bath, the metallic deposition starts immediately, thus improving the stability in aqueous media. In other words, during the electroless coating process, the particles of active material are then exposed to an aqueous environment without being protected for 1 min, which

does not seem to have an assessable impact on the performance of the cathodes made with coated particles.

Coin cells fabricated with  $\text{LiCoO}_2$  powders have shown improved performances when the active material was coated with a thin layer of metal/metal oxide by electroless deposition. The presence of copper oxide on the particles of active material has shown its effectiveness under more severe cycling conditions. The coating allows using water as a solvent in the preparation of the cathodes, leading to NMP-free manufacturing process of lithium-ion batteries. The up-scaling of the metallization process was accomplished using a Comber pilot dryer filter, and it did not influence the effectiveness of the treatment. This opens the possibility to a future implementation of the powder coating via electroless process on an industrial level.

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##### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

##### Notes

The authors declare no competing financial interest.

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