# Surveying of Electrochemical and Thermal Properties of Lithium Ion Batteries Cathode Materials Coated by $Al_2O_3$ and $ZrO_2$ using Sol-Gel Method

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---------------------------------------------------**ABSTRACT**--------------------------------------------------------

*In this study, we analyze the impact of the cathode material coating by using the sol-gel method. $ZrO_2$ and $Al_2O_3$ Layers were synthesized on the $LiNi_{0.8}Co_{0.2}O_2$ particles surface. The thickness of the layers was estimated at a theoretical value of 5µm. Suitable quantities of acetylacetonate of zirconium and aluminum isopropoxide were dissolved in acetylacetone and isopropanol as organic solvents, respectively. The solution was stirred and heated at low temperature. After a partial evaporation of the solution, the $LiNi_{0.8}Co_{0.2}O_2$ powder was immersed and the mixture was heated in air at suitable temperatures. A comparative study by x-rays diffraction was carried out on the uncoated, $ZrO_2$-coated and $Al_2O_3$-coated compounds. The electrochemical tests were performed on the three samples for the first 20 cycles. The samples in a galvanostatic charged state were analyzed by differential scanning calorimeter (DSC). The results show that the integrity of material of cathode is preserved after treatment. One observes a best cycling stability when the material is coated with $ZrO_2$ or $Al_2O_3$. For the DSC thermal analysis, we note that the exothermic reaction starts around temperature of 215°C (±8%) and that the released energy during this process is reduced approximately 40%.*

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## I. INTRODUCTION

In the lithium ion batteries, several studies showed that the main part of the electrochemical properties was due to surface properties of the electrodes [1]. J. Cho et al. have shown, by using the sol-gel technique, which it was possible to improve electrochemical and thermal properties of the positive electrodes materials by coating the particles surface with an inactive material. The structural and thermal instability of cathode materials such as $LiCoO_2$, $LiNiO_2$ and $LiNi_{0.8}Co_{0.2}O_2$ can be improved by the presence of the metal oxide protective coating. This result involved two assumptions on the surface quality of the made up one: the presence of a thin metal oxide phase on the surface or the formation of a solid solution phase between cathode material and coating metal on the surface of the particles [2]. Our work was performed with the aim of improving electrochemical behavior of cathodes materials for lithium ion batteries and especially to reduce the thermal reactions. The particles of the active compound are coated by a thin oxide coating to reduce the interaction electrode/electrolyte. Such techniques were largely used to this end. J. Cho et al., H-J. Kweon and D.G. Park [2, 3] succeeded in decreasing the exothermic reaction of positive electrode material, by coating the cathode particles by a thin metal oxide coating. The exothermic reaction was appreciably decreased when the particles surface is coated because this one limits the contact between the electrode and the electrolyte [3]. The electrochemical properties are also improved [2,3].

The studies led on the improvement of the electrochemical and thermal properties by coating $LiNi_{0.8}Co_{0.2}O_2$ particles with $SiO_x$[4] and $Al_2O_3$[5] thin layers using chemical vapor deposition (CVD), one observed a reduction in the heat released during the exothermic reaction from approximately 35% with the layer of $Al_2O_3$ and 50% for $SiO_x$. However, galvanostatic cycling was faded in both cases. The use of ZnO as thin layer showed that the start material was faded[5]. The same failure in electrochemical behavior was observed by using as coating materials the solid solution of $Li_{3x}La_{2/3-x}[]_{1/3-2x}TiO_3$[6].

In order to understand the capacity loss which we observed with CVD[4,5] and Sol-Gel[6] methods, we carried out the coating of $LiNi_{0.8}Co_{0.2}O_2$ by simple metal oxides, $Al_2O_3$ and $ZrO_2$ by Sol-Gel method. Aluminum and zirconium oxides have been widely used to improve the structural stability of positive electrode materials in lithium ion batteries [7-11]. The results obtained with alumina by CVD method, seem us to be sufficiently promising so that we test it by sol-gel method [3, 8].

In this study, we present x-rays diffraction, electrochemical and differential scanning calorimeter results of uncoated and coated material by $Al_2O_3$ and $ZrO_2$.

## II.  EXPERIMENTAL

### 2.1. Material preparation by Sol-Gel Method

Commercial powder of $LiNi_{0.8}Co_{0.2}O_2$ (Merck Company), with average particle size of 10μm, was used. The $LiNi_{0.8}Co_{0.2}O_2$ powder was synthesized at a temperature higher than 800°C and it can release electrochemically a specific capacity about 180mAh/g.

To obtain a sol-gel $Al_2O_3$ and $ZrO_2$ coating on the surface of $LiNi_{0.8}Co_{0.2}O_2$ particles, aluminum isopropoxide (98%, Aldrich) and zirconium acetylacetonate (98%, Aldrich) were dissolved in isopropoxide (99%, Aldrich) and acetylacetone (99%, Aldrich), respectively, in appropriate amounts. The appropriate amounts of precursors are obtained by a theoretical calculation of the metals oxide quantities necessary to coat surface of the $LiNi_{0.8}Co_{0.2}O_2$ particles with a thickness layer of about 5nm, for a fixed mass.

Both mixtures have been stirred at room temperature and then heated at 120°C during 2 hours in continuous stirring. The surface of $LiNi_{0.8}Co_{0.2}O_2$ particles were immersed in the coating solution such that the total amount of coating solution corresponded to 5wt% of $LiNi_{0.8}Co_{0.2}O_2$ powders. In the following step, $LiNi_{0.8}Co_{0.2}O_2$ $Al_2O_3$-coated gel was dried at 150°C and the powder obtained was fired at 600°C for 3h. The same treatment was applied with $LiNi_{0.8}Co_{0.2}O_2$ $ZrO_2$-coated gel, except that firing was led at 400°C for 3h.

### 2.2. Structural investigations

The structural characterization studies were performed by x-rays diffraction on a Philips XRD 3100 using Cu Ka radiation in a θ/2θ geometry. Parameters refinement was carried out with the U-FIT software.

### 2.3. Electrochemical Measurements

The electrochemical performance was investigated by galvanostatic charge/discharge experiments using a MacPile system (BioLogic). The cathode electrodes were formed by mixing the active material (coated and uncoated $LiNi_{0.8}Co_{0.2}O_2$ powder), the carbon black and the polyvinylidene fluoride (PVdF) dissolved in n-methyl pyrolidinone as binder, in weight ratio of weight ratio of 0.80/0.13/0.07. The electrochemical cells consisted of simple two-electrode using metallic lithium as the negative electrode. The electrolyte was a 1M solution of LiPF6 dissolved in ethylene carbonate/ diethyl carbonate (EC: DEC) 2:1 (Merck). A glass fiber paper was used as the separator and wetted with the electrolyte solution.

### 2.4. Thermal measurements

Cathode samples, for differential scanning calorimetry (DSC) analysis, were charged to 4.3V vs Li under constant current at C/16 rate. A DSC 4 Perkin-Elmer was used. The cells were then dissembled in the glove box to remove the charged cathode. Approximately 6mg of the cathode material were sealed in a sealed aluminum sample pan. Only the cathode material was used to calculation of specific heat flow, the weight of the electrolyte contained was not considered. The heating rate of the DSC experiment was 10°C/min.

## III.  RESULTS AND DISCUSSION

### 3.1. X-ray powder diffraction

Figure 1 presents X-rays diffraction patterns of $LiNi_{0.8}Co_{0.2}O_2$ uncoated (fig1a), $ZrO_2$-coated (fig1b) and $Al_2O_3$-coated (fig1c). The diagrams do not show drastic differences. Indeed, the parameters refinement of X-rays diffraction patterns by using U-FIT software showed that the treated samples remain indexed in the group of R3-m spaces in accordance with the result obtained with the sample untreated. This assertion is confirmed by the intensity ratio of the two principal indexed peaks (003) and (104) whose value is approximately 1.4 in agreement with the results obtained with $LiNi_{0.8}Co_{0.2}O_2$ $SiO_x$-coated[4]. Thus, the $LiNi_{0.8}Co_{0.2}O_2$ powder coated with $ZrO_2$ or $Al_2O_3$ by the sol-gel method under the conditions announced previously preserves the structural integrity of initial material. Two assumptions can be advanced first the thickness of the coating layer is sufficiently weak that it cannot be characterized by x-rays diffraction because of the detection limit of equipment in accordance with the results observed by Sang Myoung Lee and Al [7] or the deposited layer remains in a amorphous state undetectable by x-rays diffraction [4]. It remains to be seen if the presence of such a layer allows an improvement of the electrochemical and thermal properties of material of $LiNi_{0.8}Co_{0.2}O_2$ cathode.
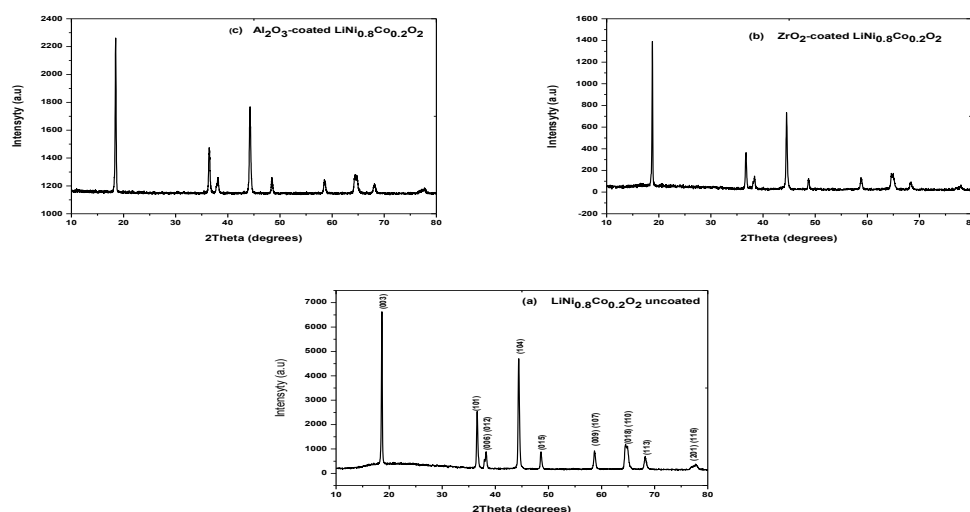
Figure 1. X-ray diffraction pattern of $LiNi_{0.8}Co_{0.2}O_2$: Uncoated (a), $ZrO_2$-coated (b) and $Al_2O_3$-coated (c)

### 3.2. Electrochemical measurements

The uncoated, $ZrO_2$-coated and $Al_2O_3$-coated $LiNi_{0.8}Co_{0.2}O_2$ samples were tested electrochemically with the aim of determining the coating effects on the electrochemical performance of the cathode material.

Figure 2 shows the cycling stability curves of the specific charge/discharges capacity over the 20 consecutive in the constant current mode of the three samples under the same experimental conditions: 0.1C rate, lithium as negative electrode, LiPF6 dissolved in EC: DEC: 2:1 (Merck) as electrolyte.

The uncoated cathode material (fig.2a) presents a first charge capacity of 195mAh/g and a first discharge capacity of 172mAh/g what gives initial capacity efficiency 88%.

In the case of $LiNi_{0.8}Co_{0.2}O_2$ coated by $ZrO_2$, the first charge and discharge capacities are respectively 199mAh/g and 172mAh/g what is equivalent to a capacity efficiency of 86% (fig.2b). When the coating material is $Al_2O_3$, the first cycle capacities are 208mAh/g for the charge and 173mAh/g for the discharge, so the capacity efficiency is 83%. We have consigned these data in table 1. The capacity retention of the uncoated material is 70% after 20 discharges cycles whereas for the coated materials the capacity retention is 88% for $ZrO_2$-coated and 91% for $Al_2O_3$-coated. So the capacity loss is more important in the uncoated material (-30%) compared to coated materials which present a capacity retention of about 90%.

Table 1. Ratio of capacity specific in the first and 20th cycles for uncoated and coated samples

| Ratio of Specific Capacities | Uncoated | $ZrO_2$-Coated | $Al_2O_3$-Coated |
|---|---|---|---|
| 1st discharge/1st Charge(%) | 88 | 86 | 83 |
| 20th discharges/1st discharges (%) | 70 | 88 | 91 |

One can note that when $LiNi_{0.8}Co_{0.2}O_2$ particles are coated by a metal oxide thin layer ($ZrO_2$ or $Al_2O_3$), the electrochemical performances are improved. However, even for the coated compounds, one notes a progressive capacity loss that predicts a rather fast deterioration of the cell to the next cycles. The rate of the capacity loss in each sample represents the influence of the protective coating on the electrochemical properties of material of cathode.

It is indeed possible to interpret the high rate of capacity loss to the first cycle of the aluminum and zirconium oxides coated compounds by the fact that the protective layer slow down the intercalation/desintercalation electrochemical diffusion process of lithium ions to take place normally thus involving a capacity loss. The presence of metal inactive oxide coating on the surface of cathode particles increases the resistance of the transfer process charge-discharge [7,8].Sang Myoung Lee et al. have showed that the protective layer coated on the surface of cathode particles obtained by solution method was non-uniform what can explain the various rates of capacity loss observed for different samples.
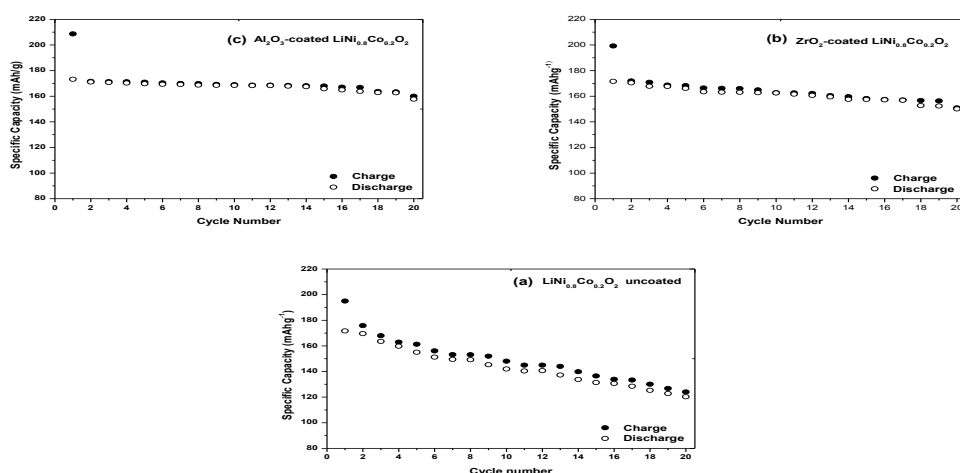
Figure 2. Cycling stability curves of charge/discharges capacities for the first 20 cycles.

In the cycling performance of the coated material the good capacity retention can be explained by the improvement of the interface stability of coated materials during cycling[12]. The formation of a solid solution to the interface allows the suppression of the transitions from structural phases observed in material of $LiNi_{0.8}Co_{0.2}O_2$ cathode. These phases transition are to the origin of the important capacity loss during cycling [10,13].

In order to establish the role of the $LiNi_{0.8}Co_{0.2}O_2$ particles coated on the exothermic reaction observed when the cathode material is in a charged state, i.e. $Li_{1-x}Ni_{0.8}Co_{0.2}O_2$, the samples studied have been charged in galvanostatic mode. A charge rate of C/16 and a voltage of cut of 4.3V have been used. La Figure 3 presents the curves obtained. The uncoated cathode material has a rate of lithium desintercalation of x=0.707 what corresponds to a specific capacity of 195mAh/g (fig3a).
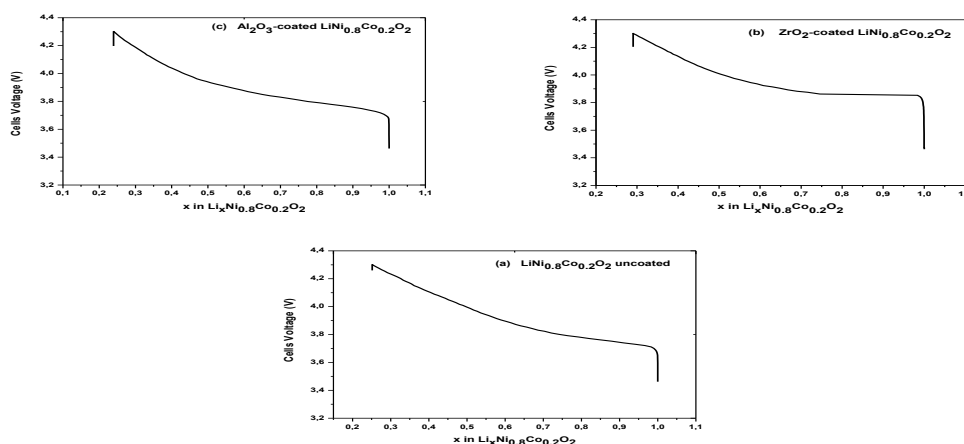


Figure 3. Galvanostatic first charge Curve: uncoated (a), $ZrO_2$-coated (b) and $Al_2O_3$-coated (c) $LiNi_{0.8}Co_{0.2}O_2$.

Under the same conditions, the coated samples show rates of lithium desintercalation of x=0.73 for $ZrO_2$ and x=0.74 for $Al_2O_3$. Their specific capacities are of 203 and 206mAh/g respectively like summary in table 2. The principal difference between the 3 curves is the presence of voltage plateau between x=0 and x=0.3 when the material is coated, thus predicting the coexistence of two phases. This result lead to a capacity loss in cycling [4,14,15]

### 3.3. Thermal measurement

One of the objectives of our study is to check the influence of the protective layer on the exothermic reaction observed when the cathode material in charged state is in contact with a liquid electrolyte [16]. The cathode electrodes at the charged state (C/16 rate, lithium as negative electrode, LiPF6 dissolved in EC:DEC: 2:1 (Merck) as electrolyte, figure 3) were sealed and test thermally by differential scanning calorimeter(DSC).

The DSC spectrums representing the heat flow variation with temperature for the charged cathode are presented in the Figure 4, for the uncoated (fig4a), $ZrO_2$-coated (fig4b) and $Al_2O_3$-coated (fig4c) samples. For the three samples, an exothermic peak is located at temperatures around 215°C with a tolerance of ±8°C, as consigned in the table 2. These temperatures are agreement with the values reported in the literature [17].
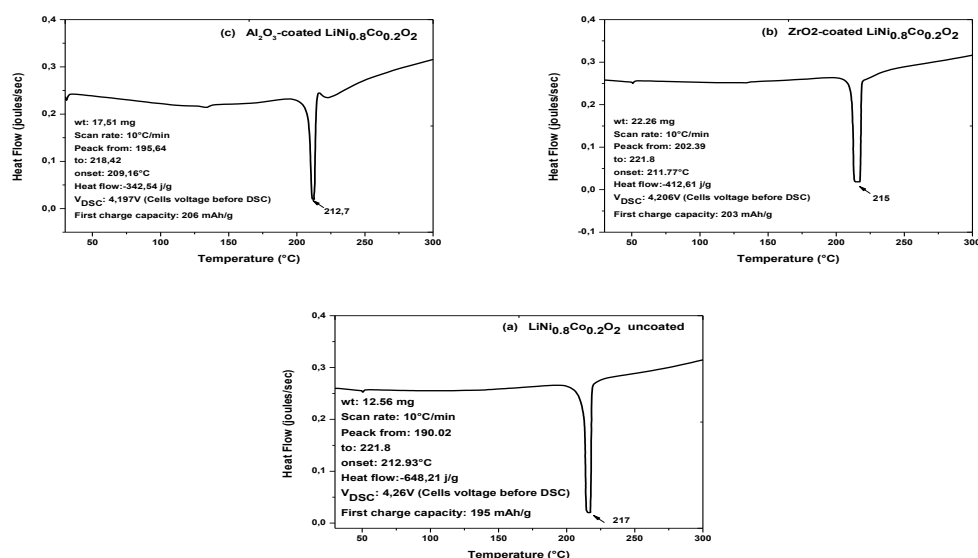
Figure 4. DSC Curves of electrodes in charged state: uncoated (a), $ZrO_2$-coated (b) and $Al_2O_3$-coated (b)

However, the intensities values of the exothermic reaction peaks are different for the three samples (table 2). The uncoated sample exhibits a energy release of about 648j/g what seems to be in conformity with the literature [4,17,18]. For the coated samples, a reduction of the exothermic reaction energy is observed. The $ZrO_2$-coated material presents an exothermic peak whose intensity is of about 413j/g whereas $Al_2O_3$-coated material releases an exothermic energy whose the value is approximately 343j/g. To take account of the mass estimation errors and the DSC calibration errors, a tolerance of ±60j/g must be taken into account for energies values obtained. These values allow a reduction in the energy of the exothermic reaction from approximately 35% for $ZrO_2$-coated sample and from approximately 45% for $Al_2O_3$-coated sample.

Table 2. DSC exothermic reactions experimental data of samples

| DSC experimental data | Uncoated | $ZrO_2$-Coated | $Al_2O_3$-Coated |
|---|---|---|---|
| 1st Charge capacity (mAh/g) | 195 | 203 | 206 |
| Cells voltage before DSC(V) | 4.26 | 4.20 | 4.197 |
| Temperature reaction (°C) | 217 | 215 | 213 |
| Energy reaction (j/g) | 648 | 413 | 343 |
| Exothermic energy variation (%) | | 64 | 53 |

The $LiNi_{0.8}Co_{0.2}O_2$ cathode particles coated by sol-gel method by using $ZrO_2$ and $Al_2O_3$ metal oxides makes it possible to decrease the energy intensity released during the exothermic reaction with the percentage of about 40%.

## IV. CONCLUSION

The x-rays diffraction results showed that of $LiNi_{0.8}Co_{0.2}O_2$ particles coated by $ZrO_2$ and $Al_2O_3$ using the sol-gel method did not deteriorate initial material. The electrochemical behavior of coated material shows appreciable results. The cyclability is improved. Capacity retention of about 90% is observed on the first 20 cycles. However, a regular capacity loss predicts of a deterioration of the electrochemical activity of the cell at approximately a hundred cycles. The DSC results too are satisfactory. They show that exothermic reaction occur at about 215°C and a reduction of the peak intensity of 40% approximately has observed for the two metal oxides used. However, extensive characterization studies remain to be realized. They will make it possible to determine the composition and the layer distribution of metal oxide formed around the particles.

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