Modifying of $LiNi_{0.8}Co_{0.2}O_2$ Cathode Material by Chemical Vapor Deposition Coating to Improve Thermal Stability

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Abstract

In this paper, we tried to find answers to safety problems due to use of transition metal oxide as positive electrodes in the lithium ion batteries. The exothermic reaction at high temperature induced by the contact between positive electrode in the charged state, such as $LiNi_{0.8}Co_{0.2}O_2$ and the liquid electrolyte solution based of LiPF6 (EC, DMC) is reduced by formation of ceramic oxide. Al_2O_3 – and ZnO-coated are synthesized on the surface of $LiNi_{0.8}Co_{0.2}O_2$ particles by chemical vapor deposition. The influences of deposit on the properties of starting material, in particular the thermal stability, are characterized by using, X-ray diffraction, electrochemical measurements and differential scanning calorimeter (DSC). Al_2O_3-coated sample show fading specific capacity during the first cycle. However, after several cycles a retention capacity is observed. ZnO-coated $LiNi_{0.8}Co_{0.2}O_2$ is inactive electrochemically as shown by X-rays diffraction pattern by the existence of two phases. With regard to DSC analysis in Al_2O_3-coated, one observe about 35% of reduction of heat flow during the exothermic reaction. The CVD method must be improved to obtain interesting results with regard to the electrochemical performances of treated material.

Keywords: lithium-ion batteries, CVD coating; alumina, layered cathode; electrochemistry, X-ray diffraction Thermal stability

1. Introduction

The increasing energy requirements for the portable equipment and transport involved a keen interest in electrochemical storage systems. Among the various accumulators types, lithium ion batteries are good candidates to become the battery of future.

The transition metals oxides to lamellate[1] and spinel[2] structure are the spearhead of lithium batteries technology. Lithium battery is composed of lithium metal as negative electrode, liquid electrolyte and lithium intercalation compounds as positive electrode. These lithium batteries deliver very high energy densities compared with the traditional storage systems like Lead, cadmium-nickel and nickel-hydride accumulators [3].

However owing to safety problems, the lithium batteries development as high power sources has been slowed down. Indeed, thermal studies showed the lithium battery components react thermically with heat release [4]. Using of nonaqueous liquid electrolyte induces safety problems which involves heat releases exothermic reactions in the negative[5] and positive electrodes materials[6].The transition metal oxides at the charged state undergo structure transformations with release of heat.

Particular attention was focused on search of new materials having low costs, a high electrochemical performances and a good thermal stability. $LiNiO_2$ and $LiMn_2O_4$ compounds were proposed to replace $LiCoO_2$ used as cathode electrode material in commercial lithium battery devices. $LiMn_2O_4$ is most stable thermically, less expensive and no toxic. Nevertheless, it presents an important loss capacity in cycling [7]. For costs reasons and electrochemical performances, $LiNiO_2$ seems to be the material which offers more potentiality compared with $LiCoO_2$. However, it is difficult to synthesize in good stoichiometry, the presence of ions nickel in the sites of driving lithium to the formulation $Li_{1-x}Ni_{1+x}O_2$ and also has an important thermal instability in the desintercaled phases [8]. Many efforts were made with the aim of reducing the metal-oxygen bond dissociation. In the $LiNiO_2$ cathode material, a partial substitution of nickel atoms by elements such as Co, Ga, Mg, Ti, Al allows to improve thermal stability while preserving good electrochemical performances[9-10]. In spite of a better thermal stability than $LiNiO_2$, the substitued compounds cannot be used in commercial systems because of safety recommendations.

Several studies were carried out with the aim of improving the physicochemical properties of materials of positive electrodes. They consist to coat the particles surface of positive electrode by some metal oxides[11-15]. These works showed an improvement of electrochemical performances and thermal stability of positive electrode materials such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and $LiNi_{0.8}Co_{0.2}O_2$ [11-17]. The formation of oxide coating around particles has as a role to reduce interaction between positive electrode and electrolytic solution. This layer must not to deteriorate the electrochemical properties of the initial compound.

The electrode/electrolyte interface being the seat of lithium ions transfer, the presence of layer on the electrode particles can slow down the diffusion of the ions. Thus, the structure and the thickness of the layer must be optimized not to deteriorate the transfer of the ions. The coated materials and the techniques used for the deposit must allow the formation of a sufficiently thin film.

Many methods of syntheses were used to coat the positive electrode particles. Among dry methods, Atomic Layer Deposition (ALD) showed good [17]. The similar results have been observed using the wet method to coat particles $LiNi_{0.8}Co_{0.2}O_2$ as reported by Jiangfeng Xiang and al.[14]. In our case, we used the chemical technique of plating in vapor phase traditional which we had already used to coat $LiNi_{0.8}Co_{0.2}O_2$ by SiO_x [11].

The aim this work is to reduce exothermic reaction occurs in the lithium ion battery when cathode electrode material is in the charged state. We have used $LiNi_{0.8}Co_{0.2}O_2$ materials as starting cathode material (obtained commercially from Merck company).il has good electrochemical performances and a energy density higher (180mAh/g) than $LiCoO_2$ (140mAh/g). In spite of a better thermal stability than $LiNiO_2$, $LiNi_{0.8}Co_{0.2}O_2$ cannot be used in commercial systems because of safety recommendations.

An attempt to synthesize thin layers of Zinc and Aluminum oxide layers were carried out on the surface of the $LiNi_{0.8}Co_{0.2}O_2$ particles using the traditional Chemical Vapor Deposition method in which a rotary system was adapted[11].

The precursors are organometallic ones which can react with the water or oxygen molecules contained in the CVD air flow to form required oxides. For Al_2O_3, we used aluminum trimethyl [$(CH_3)_3Al$, TEA] as precursors whereas ZnO precursor was the zinc diethyl [$(CH_3CH_2)_2Zn$, DEZ]. The CVD process deposition is the same one as that which we presented during our SiO_x-coated $LiNi_{0.8}Co_{0.2}O_2$ work [B]. Due to liquid state of precursors, we have carried out some adaptations in CVD system. X-rays diffraction structural characterization, galvanostatic cycling electrochemical measurements and DSC thermal analysis of uncoated and coated samples are compared and discussed. We emphasize on the structural changes and the influence of the treatment on the electrochemical and thermal properties of the covered samples.

2. Experimental

2.1. Material preparation

$LiNi_{0.8}Co_{0.2}O_2$ was a commercially available powder obtained from Merck Company and was used as-received. The characteristics of this powder are primarily its high temperature of synthesis (> 800°C) and its electrochemical specific capacity of approximately 180mAh/g.

2.2. Chemical Vapor Deposition (CVD) process

A tentative synthesis of Al_2O_3 and ZnO coating on the $LiNi_{0.8}Co_{0.2}O_2$ powder as protective layer was performed by Chemical Vapor Deposition (CVD) process. Coatings were obtained from trimethylaluminum ($(CH_3)_3Al$, TMA) and Diethylzinc ($(C_2H_5)_2Zn$, DEA) as precursors.[18] Table 1 presents the physical parameters of these compounds.

The process used is the same one as that which we used for the coating of $LiNi_{0.8}Co_{0.2}O_2$ by SiO_x [11]. Deposition parameters have been optimized in order to deposit a thin layer through which lithium ion can diffuse to reach the active material. Additionally, the Protective film must not decrease too much the electronic conductivity of the starting powder. To achieve this, we aim at the thickness below 10nm.

The deposition was performed in a stainless steel reactor heated at 300°C under vacuum. The remaining pressure before the coating treatment was between 30 and 50 mtorr.

In addition, the organometallic bottles and the ducts of connection were heated at 100°c using a thermostated bath and heating ribbons, respectively. The temperature of the ribbon was controlled using a controller of temperature. Ribbon temperature was fixed by using a controller of temperature. The goal of this operation has been to increase vapor pressure of liquid precursors and to make easy the gas flow in ducts (table 1).

Approximately 4g of $LiNi_{0.8}Co_{0.2}O_2$ powder were located in the middle of the heating zone in a rotating sample holder which allows a homogeneous deposition of the film all around the particles. Tests performed in a conventional sample holder have shown that the covering of the particles surface was only partially achieved.

Precursor was introduced in the reactor at a flow rate of 150 SCCM during 5 minutes. During the deposition, the pumping was reduced and the pressure was maintained at 5 torr. Then, the reactor was kept under vacuum and oxygen was supplied for 5 minutes at a rate of 200 SCCM. The process was repeated 10 times and the total time is about 2 hours.

2.3. Structural investigations

X-ray diffraction analysis was performed on a Philips XRD 3100 using Cu Kα radiation in a θ/2θ geometry. The X-rays parameters refinements were carried out with the U-FIT software.

2.4. Electrochemical Measurements

The positive electrodes were fabricated by mixing together active material (coated and uncoated $LiNi_{0.8}Co_{0.2}O_2$ powder), carbon black and polyvinylidene fluoride (PVdF) dissolved in n-methyl pyrolidinone as binder, with a weight ratio of 0.80:0.13:0.07. The mixture was deposited on aluminum substrates using a barcoater and dried for 12 hours at 100°C. 12mm diameter pieces of the composite electrode were cut and used as samples for both electrochemical tests.

Electrochemical tests were performed in a simple two-electrode cell using metallic lithium as the negative electrode. The electrolyte was a 1M solution of $LiPF_6$ 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. The cells were assembled in a glove box filled with argon and cycled using a MacPile system (BioLogic) in potentiostatic mode. The voltage limits and rate will be indicated when required.

2.5. 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.

3. Results and discussion

3.1. X-ray powder diffraction

Fig.1a shows X-rays Diffraction patterns of $LiNi_{0.8}Co_{0.2}O_2$ uncoated which can be indexed according to the *R-3m* space group, in the hexagonal cell [9,11,12]. The cell parameters are found to $a = 2.866(1)Å$ and $c = 14.159(6)Å$. However, this X-ray diffraction pattern refinement shows the presence of small additional peaks due to Li_2CO_3 impurities layer on the surface of $LiNi_{0.8}Co_{0.2}O_2$ particles[11,19]

As shown on the fig1b, X-Ray Diffraction of $LiNi_{0.8}Co_{0.2}O_2$ Al_2O_3-coated by CVD do not present significant modification of the starting structure. We note light changes as announced in our study on the coating of $LiNi_{0.8}Co_{0.2}O_2$ by SiO_x.[11]. The structure obtained remains indexed in same group of space as $LiNi_{0.8}Co_{0.2}O_2$ untreated.

In fig1c, X-Rays Diffraction patterns of $LiNi_{0.8}Co_{0.2}O_2$ coated with ZnO shows a change of the structure and the presence of a new phase. This result can be explained by a reaction of the precursor with starting material. Impurity peaks in X-ray diagram confirms this assumption. Impurity phase does not identify. The most intense peak of this phase, located at *43°* into *2θ* can be assigned, according to tables JCPDS, to nickel zinc compound. We can say that in the pattern, there are two phases, raw material and parasitic phase due to zinc containing.

3.2. Electrochemical measurements

The figure 2 presents the first cycles of uncoated and Al_2O_3-coated material. The cathode electrodes are charged until 4.3V vs Li. In the case of bare $LiNi_{0.8}Co_{0.2}O_2$, fig.2.a, around 0.7 of lithium were removed during the first charge and the specific capacity is 195 mAh/g at a C/16 rate. One can say with these values that the Li_2CO_3 impurity layer do not affect the electrochemical performance. In the fig.2b, about 0.6 of lithium were desintercaled from Al_2O_3-coated $LiNi_{0.8}Co_{0.2}O_2$ The first charge curves show the presence of a two-phase region during beginning of charge process.

The comparative of specific capacity between uncoated and Al_2O_3-coated samples are present in the figure 3. We observe a very regular loss capacity in cycling. For the bare sample, the efficiency capacity is 88% while the Al_2O_3-coated sample exhibits 82% efficiency capacity. One can see that in the following cycles, the coating improve the retention capacity. After 20 cycles, the efficiency capacity of uncoated and coated cathode electrode is about 93%.

This result can be interpreted like due to the presence of Al_2O_3 coating. During first charge-discharge cycle, the oxide coating performs the role of an obstacle which is difficult to climb by lithium ions, from which loss of capacity was observed. In the next cycles, the Al_2O_3 coating is more easy passes through by lithium ion and the capacity retention is better as reported by J. Cho and al.[9,12].

This improvement of the retention of the capacity can be explained by the fact that oxide coating strengthen the $LiNi_{0.8}Co_{0.2}O_2$ structure by preventing the dissolution of the cobalt and nickel atoms as indicated in the literature [11,13,14].

Since, neither X-rays diffraction nor the characterization by scanning electronic microscopy detected Al_2O_3 coating; one can conclude that the layer is sufficiently thin to not deteriorate starting material and to allow the lithium ions to cross it during the electrochemical process. However, the cyclic aspect of the evolution of the loss of capacity induces the problem of an interaction between layer deposited and ions lithium during the intercalation.

The most important point remainder the fact that this phenomenon occurs in a reversible way, which can be interpreted as a homogeneous constraint on the compound.

Consequently, we could not explain in a clear way this variation of capacity if not that the material in particular deposited oxide Al_2O_3 aluminum interacts with the reversible lithium of way.

The electrochemical test of ZnO-coated $LiNi_{0.8}Co_{0.2}O_2$ is in accord with the X-rays diffraction results (fig.1c). As shown in the figure 4, ZnO-coated sample is not electrochemically active in the range of potential used. This result was observed on several samples in the same condition. As shown in fig.1c, there is reaction between $Zn(CH_3CH_2)_2$ and $LiNi_{0.8}Co_{0.2}O_2$ particles which results in the impossibility to desintercale the lithium ions. It seems that ZnO-coated was very thick and prohibited the diffusion of lithium ions out of $LiNi_{0.8}Co_{0.2}O_2$.

3.3. Thermal measurement

X-rays diffraction and electrochemical measurement of ZnO-coated $LiNi_{0.8}Co_{0.2}O_2$ were given poor results; so, differential scanning calorimeter (DSC) measurements were carried out only on the Al_2O_3-coated $LiNi_{0.8}Co_{0.2}O_2$ electrode.

Figure 5 presents DSC curves of uncoated and Al_2O_3-coated $LiNi_{0.8}Co_{0.2}O_2$. Galvanostatic cycling conditions assume that the electrodes are charged to 4.3 at C/16 rate. One notices a significant reduction in the exothermic reaction for Al_2O_3-coated (fig.5b). These tests were carried out on several samples of this type and the results always showed a reduction of exothermic peaks.

One can also highlight that the exothermic reaction in Al_2O_3-coated sample occur at 203±8°C (fig.5b) while uncoated sample exhibit exothermic peak at 222±8°C (fig.5a). This result is in agreement with the values reported in literature [11, 20, 21]. The heat flow for bare $LiNi_{0.8}Co_{0.2}O_2$ display 490 ± 60J/g value while Al_2O_3-coated $LiNi_{0.8}Co_{0.2}O_2$ exhibit 320 ± 60J/g. The heat value of uncoated cathode electrode is lower that literature values.[22,23].The presence of Al_2O_3 coating on the surface induces a reduction of the exothermic reaction from approximately 35% compared to the heat loss by the bare compound.

4. Conclusion

ZnO-coated powder process shows a reaction with $LiNi_{0.8}Co_{0.2}O_2$ which results to the presence of impurities peaks in X-rays diffraction pattern and the absence of an electrochemical activity. It can assume that ZnO layer prevented diffusion of lithium ions out of $LiNi_{0.8}Co_{0.2}O_2$. In the case of Al_2O_3-coated $LiNi_{0.8}Co_{0.2}O_2$, we have better results, comparable with those obtained for silane. When Al_2O_3 coating is performed, structural analysis show that the properties of coated material are not modified. On the other hand, electrochemical measurements show similar behavior with SiO_x-coated $LiNi_{0.8}Co_{0.2}O_2$, namely the presence of a plate at the beginning charge cycle[11]. The biphasic region seems to come from the interaction between initial material and coating thin film which would generate $Li(Ni_{0.8}Co_{0.2})_{1-y}M_yO_2$ solid solution type where M represents Al and Zn. This assumption was already underlined by J. Cho et al. and seems most plausible to explain the presence of a biphasic region.

The regular loss of the specific capacity in cycling predict a phenomenon which proceeds in a reversible path, but the actual position of our work does not allow to identify it clearly. There can be due to phenomena induced by the $LiNi_{0.8}Co_{0.2}O_2/Al_2O_3$ interface. And yet, the coating material process allows a reduction of the exothermic reaction from approximately 35%. Nevertheless, one thinks that a refinement of CVD deposit parameters remains necessary to understand what happens.

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Table 1. The physical parameters of precursor compounds

Precursors compound	FW (g/mol)	Boiling point (°C)	Melting point (°C)	Density at 25°C (g/ml)
Trimethylaluminum $(CH_3)_3Al$ (TMA) à 97% (Aldrich)	72,09	125 - 126	15	0.752
Diethylzinc $(C_2H_5)_2Zn$ (DEZ) (Aldrich)	123,49	117°C	-28°	1.205

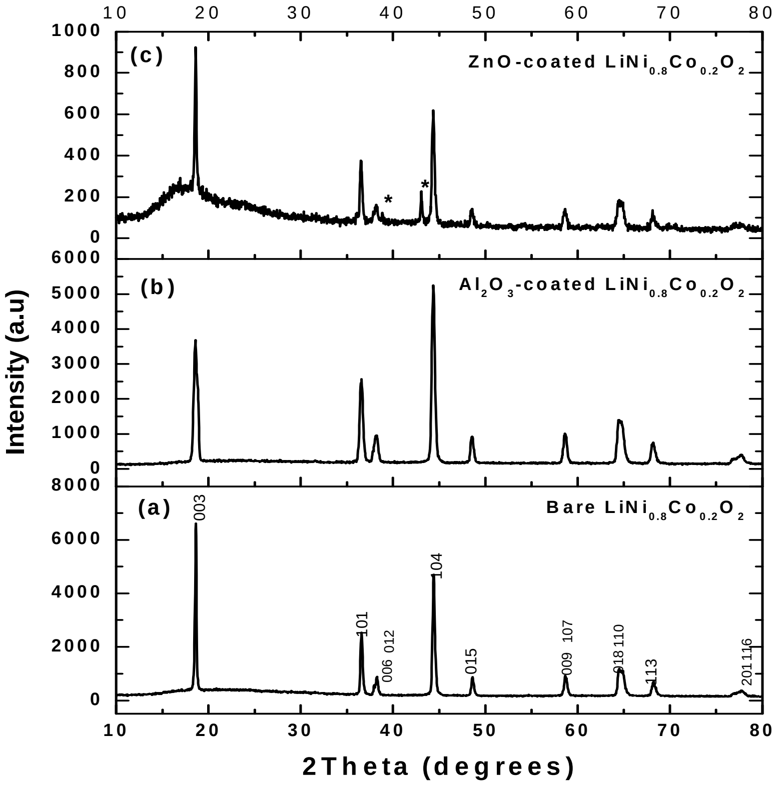

Figure 1. X-ray diffraction pattern of $LiNi_{0.8}Co_{0.2}O_2$ powder: (a) Bare, (b) ZnO-coated (c) Al_2O_3-coated

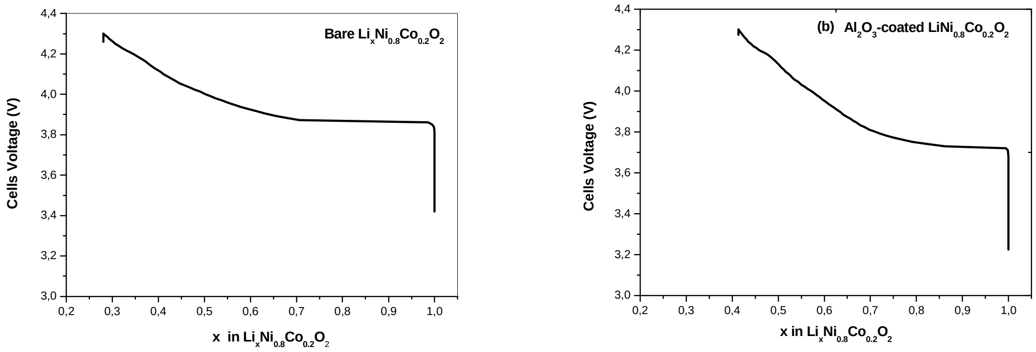

Figure 2. Galvanostatic Curves of the first charge for (a) bare and (b) Al_2O_3-coated $LiNi_{0.8}Co_{0.2}O_2$ [C/16 rate, lithium as negative electrode, $LiPF_6$ dissolved in EC:DEC: 2:1 (Merck) as electrolyte].

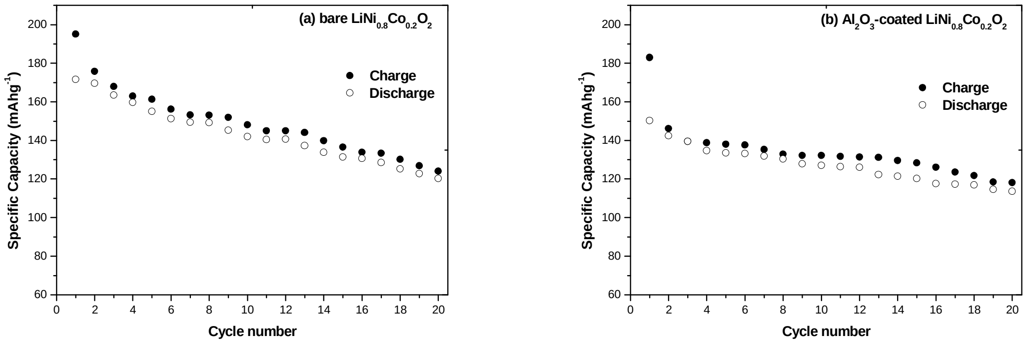

Figure 3. Variation of the specific charge/discharges capacity over the 20 consecutive in the constant current mode: (a) bare and (b) Al_2O_3-coated $LiNi_{0.8}Co_{0.2}O_2$ [C/10 rate, lithium as negative electrode, $LiPF_6$ dissolved in EC:DEC: 2:1 (Merck) as electrolyte].

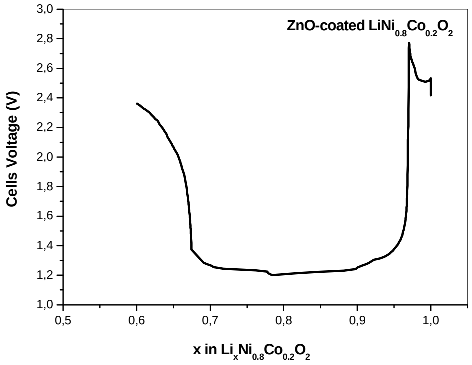

Figure 4. Galvanostatic Curve of the first charge of Zn-coated $LiNi_{0.8}Co_{0.2}O_2$ [C/16 rate, lithium as negative electrode, $LiPF_6$ dissolved in EC:DEC: 2:1 (Merck as electrolyte].

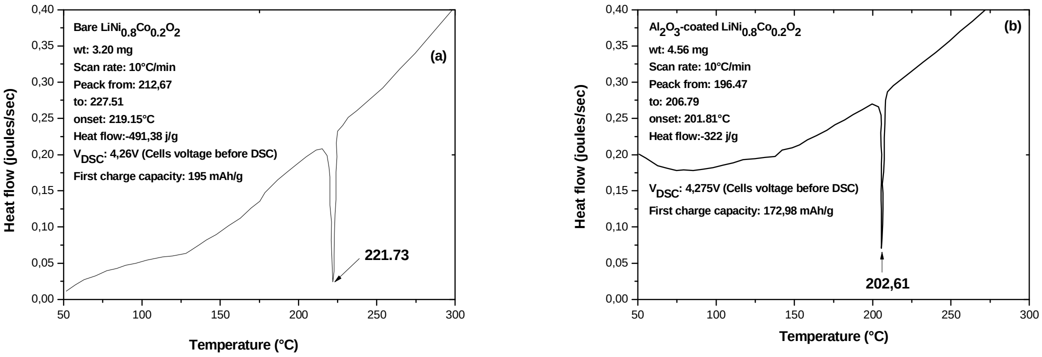

Figure 5. DSC Curves of electrodes in the charged states: (a) bare and (b) Al_2O_3–coated $LiNi_{0.8}Co_{0.2}O_2$.

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