

# Moisture-uptake by the positive active material from the casting solvent and the ambient environment

Vijay Saharan<sup>a,\*</sup>, Jeffrey Roberts<sup>a</sup>, Vesselin Manev<sup>a</sup>, Yee Ho Chia<sup>a</sup>,  
Greg MacLean<sup>b</sup>, Steven R. McMullen<sup>b</sup>

<sup>a</sup> Technical Center Flint, Delphi Energy & Chassis Systems, 1601 N. Averill Avenue, Flint, MI 48556, USA

<sup>b</sup> Delphi Energy & Chassis Systems, 8750, Hague Road, Indianapolis, IN 46256, USA

Available online 26 April 2005

## Abstract

It is widely recognized that the presence of residual moisture has significant detrimental effects on the performance of lithium ion batteries. Studies have shown that the positive active material can be a major source of moisture contributors to the overall cell moisture. The aim of the present study is to understand the factors affecting moisture uptake by the doped-lithium nickel cobalt oxide material from the casting solvent, acetone, and the ambient environment. As-is and the air-dried powders under various conditions (300 °C for 24 h, 500 °C for 8 h, and 500 °C for 24 h) were exposed to ambient and humid air for various lengths of time. Similarly, all these powders were exposed to extra dry (47 ppm) and wet (5789 ppm) acetone. Karl Fisher measurements at 160 °C and 290 °C show that humidity levels (80–85% relative humidity versus 20–25%) and the exposure times are the critical factors. Acetone wetness and the length of exposure in it do not contribute significantly to the moisture uptake by the active material. Cathode powder drying helps in minimizing the amount of moisture uptake from the environment. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Moisture; Doped-lithium nickel cobalt oxide cathode; Acetone; Ambient conditions; Humid environment; Lithium battery

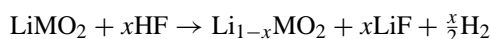
## 1. Introduction

Presence of moisture is widely known to have significant detrimental effects on the battery performance for capacity, power, cycle life, and calendar life in lithium ion battery technology. Various reaction mechanisms have been proposed to explain the effects of moisture on the electrolyte, negative electrode, positive electrode, and overall cell chemistry. For the electrolyte, it is commonly accepted that the moisture reacts with lithium salts, e.g. LiPF<sub>6</sub>, currently used in commercial lithium ion batteries, according to the following reaction [1]:



HF generated from the above reaction, possibly reacts with the lithium metal oxide cathode as per the following

reaction:



It is commonly accepted now that Mn dissolution for lithium manganese oxide especially at elevated temperature is induced by acids generated through temperature-enhanced electrolyte decomposition, or by water contamination of the cell components either present in the electrolyte/cell components or introduced during the manufacturing/assembly cell process, and finally due to the secondary chemical reactions occurring at the LiMn<sub>2</sub>O<sub>4</sub>/electrolyte interface [2–4].

Electrolyte manufacturers have recognized this challenge in manufacturing electrolyte solutions to minimize the contamination levels to improve the battery quality [5]. Studies on contamination levels, influence of packaging, high temperature storage, and handling have been carried out in details. A complete understanding of the SEI layer formation on the negative electrode such as carbon based material, used in lithium-ion batteries, continues to be a challenging issue. Effect of different amounts of water, as well as oxygen, in

\* Corresponding author. Tel.: +1 810 257 8936; fax: +1 810 257 2001.  
E-mail address: [vijay.saharan@delphi.com](mailto:vijay.saharan@delphi.com) (V. Saharan).

the electrolyte on the SEI layer formation on the graphite surface has been studied [6]. It was concluded that the presence of water increases the irreversible capacity loss in the first cycle due to water reduction. In later studies, it is further demonstrated that an effective and a better quality SEI layer is formed on the carbon surface when water contamination is avoided. The improved SEI layer helps in achieving high specific capacity ( $\sim 360 \text{ Ah kg}^{-1}$  of carbon), satisfactory cycle life of the graphite electrodes (1000 deep cycles), and an irreversible capacity loss of  $<7\%$  during the first cycle using  $1 \text{ M LiPF}_6$  in EC/DMC electrolyte [7]. In an attempt to understand the reduction products of ethylene carbonate, a widely used co-solvent in electrolytes for lithium-ion batteries, an electrochemical–chemical sequence of reactions has been suggested [8]. Electrochemical reduction of water to form hydroxides, and hydroxide addition to form ethylene oxide and lithium bicarbonate are some of the possible products of these reactions.

Our previous study has shown that depending upon the composition of the positive active material like lithium manganese oxide, lithium cobalt oxide, or doped lithium nickel cobalt oxide; the positive active material can be one of the major contributors to the overall moisture in the cell [9]. It was concluded that the final cell moisture content is strongly affected by the processing of films used to fabricate the cells. To minimize the moisture exposure, the commercial lithium-ion and/or lithium-ion polymer makers use dry room with controlled temperature and humidity to fabricate films and assemble the cells.

The most common film fabrication method, either directly on a metal foil or as a freestanding film is solvent casting. Typically the active material, along with a polymer binder and conductive carbon, is suspended in an organic solvent to make slurry. Acetone, due to its low cost, ease of handling, and less toxic nature is also used to cast both electrode films. However, there is always a concern that the positive active material could absorb/adsorb moisture from the acetone, consequently increasing the moisture in the film and the cell even after the cell has been subjected to some drying process. The positive active material can also pick up moisture from the environment depending upon the temperature and humidity of the ambient conditions. Doped-lithium nickel oxide materials are known to be hydrophilic in nature due the presence of excess, unreacted lithium salts on their surface. The main purpose of this study is to understand the factors and further to quantify the amount of moisture uptake from the casting solvent, i.e. acetone (dry and wet) and from the ambient air-conditions under varying temperature and humidity levels.

## 2. Experimental

Doped- $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  was dried in air using three different conditions:  $300^\circ\text{C}$  for 24 h,  $500^\circ\text{C}$  for 8 h, and  $500^\circ\text{C}$  for 24 h [10]. Karl Fisher titration method was used to measure the moisture for two heating temperatures up to  $160^\circ\text{C}$  and

$290^\circ\text{C}$ . As-is and three dried powders were exposed to the ambient conditions ( $25\text{--}30\%$  relative humidity at  $70 \pm 2^\circ\text{F}$ ) and humid conditions where relative humidity was maintained at  $80\text{--}85\%$  at  $80 \pm 2^\circ\text{F}$ . All four powders were exposed to the above-mentioned two conditions for 3 h, 6 h, and 24 h time period. For the acetone exposure experiment, ACS grade acetone containing 5789 ppm moisture and extra dry acetone obtained from ACROS ORGANICS containing 47 ppm moisture were used. All four powders were exposed in dry and wet acetone for 6 h, 24 h, 48 h, and 192 h in a sample vial. After the exposure time, acetone was decanted off and the powder in the sample vial was subjected to drying at  $60^\circ\text{C}$  for about 16 h, and then put under vacuum at the same temperature for additional 6 h to make sure that all the acetone has been removed before doing the moisture measurements. Each data point is average of two measurements.

## 3. Results and discussion

### 3.1. Effect of ambient conditions on the moisture uptake

Various time intervals for the exposure were chosen considering the practical aspect that in a manufacturing environment, it will be highly desirable to use a dried powder as soon as possible and not let it sit in a humid environment for more than 24 h. Fig. 1 shows the Karl Fisher measurements at  $160^\circ\text{C}$  for as-is and dried powders under ambient and humid conditions. It is believed that the measurements done at  $160^\circ\text{C}$  represent the loosely/weakly bound water or the physisorbed water and measurements done at  $290^\circ\text{C}$  represent a total of weakly and strongly bound water or the combination of physisorbed and chemisorbed water. The data show that the dried powders absorb/adsorb less moisture than as-is

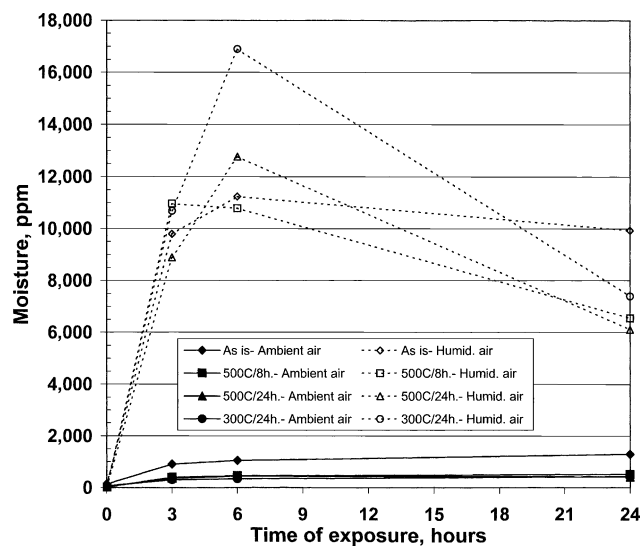


Fig. 1. Moisture measurements at  $160^\circ\text{C}$  for humid and ambient air exposed samples.

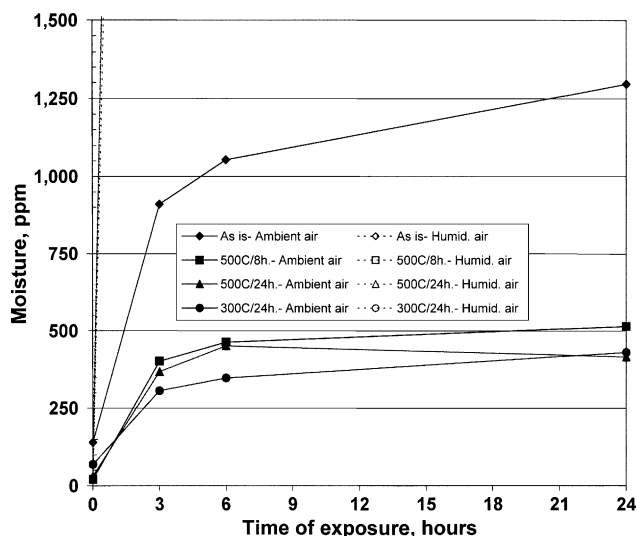


Fig. 2. Moisture measurements at 160 °C for humid air exposed samples only.

material from ambient and humid air. In a humid air environment, most of the moisture uptake happens during the first 3 h time period. Though the moisture levels are highest for all four powders after 6 h exposure, there appears some decrease of moisture when exposed for longer time up to 24 h. This phenomenon is still not well understood. It is possible that some chemical reactions involving  $\text{CO}_2$  and other components in the air can react with the cathode surface impurities to cause this decrease in moisture. All the dried powders show moisture levels in the range of 6000–7500 ppm as compared to about 10,000 ppm for the as-is material.

Fig. 2 shows the expanded graph for the ambient air only exposed samples. Majority of the moisture pick up occurs up to 6 h exposure and it is fairly constant up to 24 h exposure, at least for the dried powder. Clearly, 24 h dried powders either at 300 °C or 500 °C show less moisture after 24 h exposure (about 425 ppm) than 8 h dried powders at 500 °C (about 515 ppm). So the longer drying time is more important than the drying temperature.

Fig. 3 displays the Karl Fisher analysis done at 290 °C for as-is and three dried powders. Upon exposure to ambient air, the moisture of the dried samples levels off around 1000 ppm after 24 h exposure as compared to about 2500 ppm for the undried material. These 290 °C Karl Fisher moisture levels are about double those from the 160 °C measurement as shown in Fig. 2 for the respective powders after the same exposure time period (24 h). This suggests that longer exposure (24 h) of powder under ambient air conditions contributes not only to loosely bound water but also equally to the strongly bound water on the positive active material powder. On the contrary, humid air exposed samples for 24 h show the moisture content in the range of 7000–9000 ppm, which is about the same as the moisture analysis at 160 °C as shown in Fig. 1 indicating that in a humid environment, most of the moisture uptake is loosely bound.

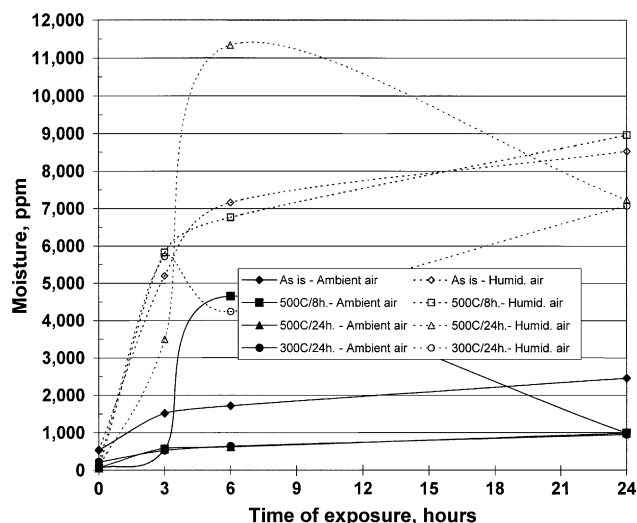


Fig. 3. Moisture measurements at 290 °C for humid and ambient air exposed samples.

### 3.2. Effect of wet and dry acetone on moisture uptake

ACS grade acetone from Fisher Scientific (considered to be wet acetone) and extra dry acetone from ACROS ORGANICS showed 5789 ppm and 47 ppm moisture levels respectively based on the 160 °C Karl Fisher measurement, where the acetone was directly injected into the titration solution of the instrument. Four different exposure times, 6 h, 24 h, 48 h, and 192 h (8 days) were selected to study the effects of time on the moisture uptake. Considering the practical aspect of casting films, it is highly desirable to use slurry as soon as possible (within 24–48 h) and not let it be stored for more than 8 days. Fast usage of the slurry to cast films can potentially have a direct impact on the turn around time for the equipments involved, improved efficiency of the operation, and therefore, lower battery cost.

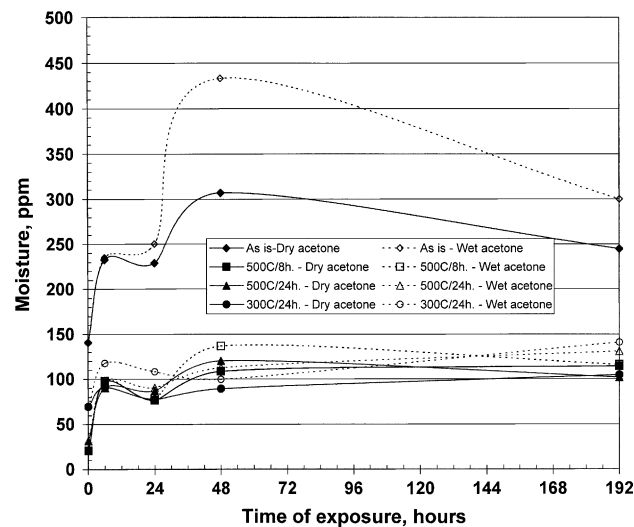


Fig. 4. Moisture measurements at 160 °C for dry and wet acetone exposed samples.

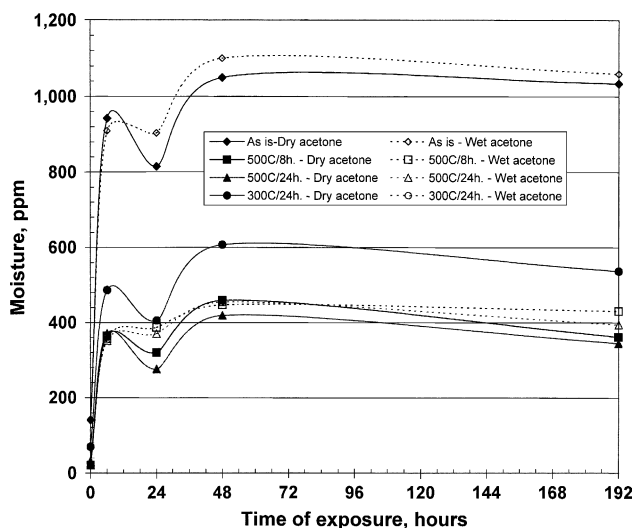


Fig. 5. Moisture measurements at 290 °C for dry and wet acetone exposed samples.

Fig. 4 shows the moisture analysis at 160 °C for the powders after these were exposed to dry and wet acetone. In general, dried or undried powders do not pick up any significant amount of moisture from either dry or wet acetone, even up to 8 days of exposure. In almost all the cases, the moisture levels increase to two to three times as compared to their respective moisture content at the 0 h exposure level or the fresh sample. Just like the ambient conditions, moisture adsorption/absorption by the dried powders is less than the as-is sample. It is also important to note that the drying time and temperature are not very critical factors. Loosely bound moisture uptake from acetone can be minimized as long as there is some drying of cathode powder at least to 300 °C for 24 h.

Fig. 5 shows the moisture content at 290 °C Karl Fisher for all the powders. At the end of 192 h (8 days) exposure, the moisture content at this temperature is almost four times higher than 160 °C Karl Fisher measurements for the respective powders as shown in Fig. 4. This observation suggests

that there is some water from acetone, which binds tightly on the active material. Among the dried samples, even at this higher analysis temperature, drying time and temperature are not very important factors.

#### 4. Conclusions

A strong interaction between the doped-lithium nickel cobalt oxide positive material and the moisture from the processing media and the processing environment was found. Humidity levels and the exposure times in the ambient environment are the critical factors in controlling the material's contamination due to moisture. However, some degree of drying the doped-lithium nickel cobalt oxide material may significantly reduce the amount of moisture uptake from the environment. Furthermore, acetone wetness and length of exposure of the active material in it does not contribute significantly to moisture uptake.

#### References

- [1] C.G. Barlow, *Electrochem. Solid-State Lett.* 2 (1999) 362.
- [2] A. Blyr, C. Sigala, G.G. Amatucci, D. Guyomard, Y. Chabre, J.-M. Tarascon, *J. Electrochem. Soc.* 145 (1998) 194.
- [3] D.H. Jang, Y.J. Shin, S.M. Oh, *J. Electrochem. Soc.* 143 (1996) 2204.
- [4] G.G. Amatucci, A.D. Pasquier, A. Blyr, T. Zheng, J.-M. Tarascon, *Electrochim. Acta* 45 (1999) 255.
- [5] U. Heider, R. Oesten, M. Jungnitz, *J. Power Sources* 81–82 (1999) 119.
- [6] F. Joho, B. Rykart, R. Imhof, P. Novák, M.E. Spahr, A. Monnier, *J. Power Sources* 81–82 (1999) 243.
- [7] P. Novák, F. Joho, M. Lanz, B. Rykart, J.-C. Panitz, D. Allia, R. Kötz, O. Hass, *J. Power Sources* 97–98 (2001) 39.
- [8] X. Zhang, J.K. Pugh, P.N. Ross Jr., *Electrochem. Solid-State Lett.* 4 (2001) A82.
- [9] Y.H. Chia, L. Pederson, M. Parsian, J. Jones-Coleman, F. Kennard, 11th International Meeting on Lithium Batteries, Monterey, CA, USA, June 23–28, 2002, Abstract no. 367.
- [10] V. Manev, V. Saharan, Y.H. Chia, J. Roberts, US Patent Pending.