

Short communication

## In situ study on CO<sub>2</sub> evolution at lithium-ion battery cathodes

J. Vetter\*, M. Holzapfel, A. Wuersig, W. Scheifele, J. Ufheil, P. Novák

*Paul Scherrer Institute, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland*

Available online 14 June 2006

### Abstract

This study based on in situ differential electrochemical mass spectrometry (DEMS) in model cells with Li(Ni, Co, Al)O<sub>2</sub> and Li(Ni, Mn, Co)O<sub>2</sub> cathodes highlights various influence parameters on CO<sub>2</sub> evolution in lithium-ion batteries. The amount of CO<sub>2</sub> formation is increased by high temperatures and cell voltages, while the addition of vinylene carbonate (VC) decreases it. Lithium carbonate present in the cathode causes increased CO<sub>2</sub> formation in the initial cycles but has little influence during prolonged cycling. Two processes of CO<sub>2</sub> formation with different kinetics could be distinguished. The amount of CO<sub>2</sub> evolved depends strongly on the type of cathode active material.

© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Lithium-ion batteries; CO<sub>2</sub> evolution; Influence parameters; Cathode materials; DEMS; Kinetics

### 1. Introduction

Gas evolution during storage and use is a major failure mechanism of lithium-ion batteries. Gases formed in the hermetically sealed cells may lead to internal pressure build-up and cell bulging, de-lamination of the electrodes and de-contacting of active material. This results in an inhomogeneous current distribution over the area of the electrodes. Oxidic active materials at the positive electrode may experience increased degradation and particle cracking under the high local current density. At the carbonaceous negative electrode, high local currents may promote lithium plating and corrosion, consuming electrolyte and irreversibly lowering the amount of lithium available for the reversible charge–discharge reaction. Lithium corrosion is associated with the decomposition of the electrolyte, increasing the internal cell resistance by deposition of low-conductive decomposition products on the electrodes, thus lowering the rate capability and power of the cell. Both, consumption of lithium and degradation at the positive electrode, reduce the available energy of the cell, while de-lamination reduces the accessible electrode area, further reducing the usable energy. Under certain circumstances lithium dendrites may be formed on the negative electrode, short-circuiting the cell and leading to pre-mature cell failure.

During prolonged storage, especially at elevated temperature and high cell voltage, i.e., in the charged state, CO<sub>2</sub> is the main

gaseous compound formed [1,2]. According to previous investigations, CO<sub>2</sub> is mainly formed at the positive electrode due to oxidation of the electrolyte [2,3]. In this study we present recent investigations, mainly based on differential electrochemical mass spectrometry (DEMS), on the conditions influencing the formation of CO<sub>2</sub> at Li<sub>1-x</sub>(Ni, Co, Al)O<sub>2</sub> and Li<sub>1-x</sub>(Ni, Mn, Co)O<sub>2</sub> electrodes in an ethylene carbonate (EC)/propylene carbonate (PC)/dimethyl carbonate (DMC), LiPF<sub>6</sub> electrolyte. The influence of cell voltage, temperature, and amount of inorganic carbonate present in the electrode is investigated in situ during CV experiments.

### 2. Experimental

With the differential electrochemical mass spectrometry (DEMS) technique it is possible to detect the different gaseous reaction products that are evolved during cycling. Hence, intensity changes in mass signals can be detected as a function of time and/or potential and, thus, can be correlated with current peaks in the cyclic voltammogram or plateaus on galvanostatic charging/discharging curves.

In this work DEMS was used to study the processes of electrolyte decomposition and to follow the formation of gaseous reaction products, especially CO<sub>2</sub>, on oxide electrodes during the first electrochemical cycles.

The amounts of CO<sub>2</sub> produced by the oxidative decomposition of electrolyte solvents at the positive electrode materials are significantly smaller than, e.g., the amounts of gases evolved from the negative electrodes during the formation of the solid

\* Corresponding author. Tel.: +41 56 310 2165; fax: +41 56 310 2078.  
E-mail address: [jens.vetter@psi.ch](mailto:jens.vetter@psi.ch) (J. Vetter).

electrolyte interface (SEI). To detect these small amounts of gases, the previously used DEMS measurement cell [4], had to be considerably improved.

The new measurement system is described elsewhere [5–7]. It is based on headspace analysis. The gaseous reaction products are pumped off continuously from the top of the electrochemical cell via a capillary into a quadruple mass spectrometer where they are analyzed on-line. With this electrochemical cell it is possible to identify even very small quantities of gas. The cell is also equipped with a heating unit for measurements at elevated temperature.

Since  $\text{CO}_2$  readily reacts with lithium to form carbon, further decreasing the already small amount of  $\text{CO}_2$  formed during electrochemical cycling, the use of metallic lithium as the counter electrode is not appropriate. For this reason a graphite counter electrode was used for the measurements. The electrodes were balanced to be limited by the positive electrode active mass, with an excess of 30% on the graphite side, in order to avoid undesired side reactions at the negative electrode due to lithium plating. The electrodes were prepared by blade-coating the oxide and graphite directly on the titanium body of the DEMS cell. For the oxide electrodes a mixture of 86.2 wt.% active material, 7.4 wt.% TIMREX KS6 graphite (TIMCAL SA, Bodio, Switzerland), 1.4 wt.% Super P carbon black (TIMCAL SA, Bodio, Switzerland) and 5 wt.% poly(vinylidene difluoride) binder (SOLEF 6020, Solvay SA, Belgium) was used. For the graphite counter electrode 95 wt.% active material were mixed with 5 wt.% poly(vinylidene difluoride) binder (SOLEF 6020, Solvay SA, Belgium). In both cases the slurries were prepared in *N*-methyl pyrrolidone. After the coating of the electrode material the cell parts were vacuum-dried at 120 °C over night. The measurements cell was assembled in an argon filled glove-box with a moisture and oxygen level of less than 5 ppm. During the measurements a constant stream of argon is flown through the headspace of the cell. Gases evolved at the electrode arise within the electrolyte to the headspace where they are pumped off, together with the argon carrier gas, via a capillary to the mass spectrometer. EC/PC/DMC,  $\text{LiPF}_6$  was used as the electrolyte for the DEMS experiments. All materials used in the test cells, including the electrolyte, were of battery grade purity.

All DEMS measurements were carried out potentiodynamically either at room temperature or 60 °C. For high temperature measurements at 60 °C ( $\pm 0.5$  °C), two separately controlled heating plates were mounted at the front and the back of the cell. A scan rate of  $400 \mu\text{V s}^{-1}$  was used for cycling voltammetry (CV). The CV measurements were started at open circuit potential (OCP; usually about 0 V). Unless otherwise stated, the cell voltage was increased from OCP to 4.3 V in the first cycle, and then varied between 4.3 and 3.0 V. For part of the measurements, a potentiostatic hold period was introduced both at the upper and lower voltage limit. These measurements allow some conclusions on the kinetics of  $\text{CO}_2$  evolution in the charged and discharged state of the battery, respectively. The current (cyclic voltammogram) and mass signals (mass spectrometric cyclic voltammogram, MSCV) were recorded simultaneously both as a function of cell voltage and time.

Mass signals were recorded on a Prisma QME 200 quadrupole mass spectrometer (Balzers AG/Pfeiffer Vacuum). Electrochemical measurements were performed using standard laboratory test equipment (Astrol AG, Amel Instruments).

### 3. Results and discussion

#### 3.1. Cell voltage and temperature

Investigations using  $\text{Li}(\text{Ni}, \text{Co}, \text{Al})\text{O}_2$  (LNCAO) as the positive active material showed a strong influence of the temperature on the onset voltage of  $\text{CO}_2$  evolution (Fig. 1). For these experiments, 3% of  $\text{Li}_2\text{CO}_3$  was added to the electrode, and the cell voltage had to be increased up to 5.1 V in order to get a  $\text{CO}_2$  signal, at room temperature, sufficiently high for analysis. Nevertheless,  $\text{CO}_2$  evolution (in the first cycle) only starts at a cell voltage of 4.9 V during the decreasing of the voltage, continuing until a cell voltage of ca. 3.3 V is reached. On the other hand, at 60 °C the  $\text{CO}_2$  evolution already starts at ca. 3.5 V while increasing the voltage, continuing until a cell voltage of 5.1 V is reached, and on the way back down to ca. 3.4 V. From these results a decrease in the onset voltage for  $\text{CO}_2$  evolution of ca. 1.4 V can be derived. As could have been expected, the overall amount of  $\text{CO}_2$  generated is higher at elevated temperatures, indicated by higher ion currents in the MS.

#### 3.2. Prolonged cycling

The evolution of  $\text{CO}_2$  upon prolonged CV cycling between 3.0 and 4.3 V was monitored for LNCAO without added  $\text{Li}_2\text{CO}_3$  at 60 °C. The correlation between the cell voltage and the  $\text{CO}_2$  evolution can be clearly recognized from the depiction of ion current and cell voltage versus time (Fig. 2). During each cycle, the  $\text{CO}_2$  evolution increases during the increase of the voltage, reaches a maximum shortly after the maximum voltage is passed, and decreases until the next CV cycle begins. The  $\text{CO}_2$  mass signal reaches a value similar to the value for propylene formation due to electrolyte decomposition during the first cycle

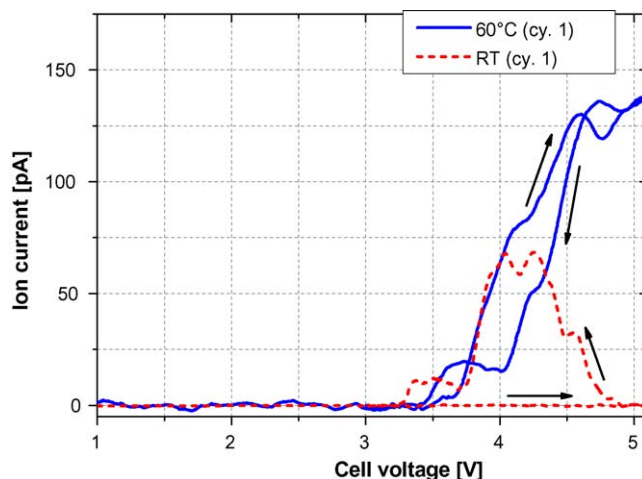


Fig. 1.  $\text{CO}_2$  evolution in cells with LNCAO+3%  $\text{Li}_2\text{CO}_3$  cathodes and EC/PC/DMC,  $\text{LiPF}_6$  electrolyte at room temperature and at 60 °C.

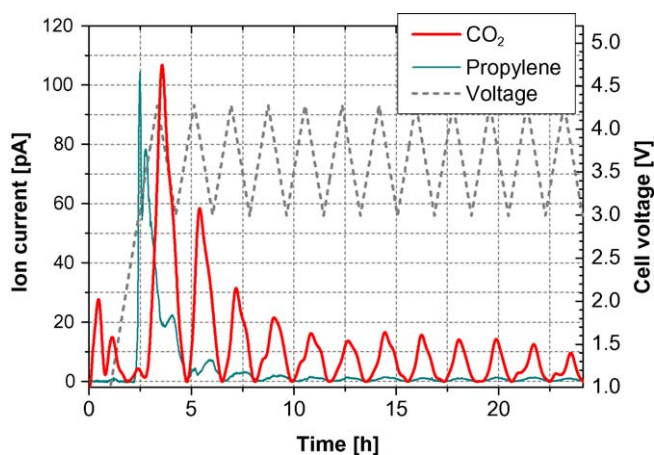


Fig. 2. CO<sub>2</sub> and propylene evolution in cells with LNCAO cathodes and EC/PC/DMC, LiPF<sub>6</sub> electrolyte at 60 °C during prolonged CV cycling.

and decreases upon prolonged cycling. The respective propylene signature is also given in Fig. 2. Although the method cannot be assumed to be quantitative when comparing different gases, this indicates that the amount of the two gases is in the same order of magnitude. Nevertheless, while propylene gas formation drops to almost zero within the first few cycles, the CO<sub>2</sub> evolution in each cycle shows a much slower decay and seems to approach a small but constant value. This is consistent with the observation of a slow but continuous pressure build-up in commercial cells during storage at elevated temperature in the charged state. Two possible explanations may be considered for the decay in CO<sub>2</sub> evolution. Firstly, a (trace) compound or impurity may be consumed during the initial cycles, reaching an equilibrium after a few cycles, either by diffusion or similar processes, or by re-formation of the compound during electrochemical cycling. Secondly, this behavior may be explained by the formation of a(n) (imperfect) passivating protective layer, which reduces the rate of the CO<sub>2</sub> formation reaction but doesn't inhibit it completely.

### 3.3. Influence of lithium carbonate

By adding different amounts of Li<sub>2</sub>CO<sub>3</sub> to the positive electrode, we investigated the influence of inorganic carbonate on CO<sub>2</sub> evolution. Lithium carbonate is present as a trace impurity in many commercial positive active materials. It is formed by reaction with atmospheric CO<sub>2</sub> according to Eq. (1) when lithium transition metal oxides are exposed to air during synthesis, packaging, shipping, or storage:



In order to get a deeper insight into the role of lithium carbonate in CO<sub>2</sub> evolution during cycling or storage, LNCAO was ball-milled with various amounts of Li<sub>2</sub>CO<sub>3</sub>. Electrodes were prepared as described above, and DEMS experiments were carried out at 60 °C. The experiments were performed potentiodynamically between 3.0 and 4.3 V. The area under the MSCV curves were integrated and plotted versus cycle number (Fig. 3). In cells with 1 and 2% of added Li<sub>2</sub>CO<sub>3</sub>, the CO<sub>2</sub> evolution in

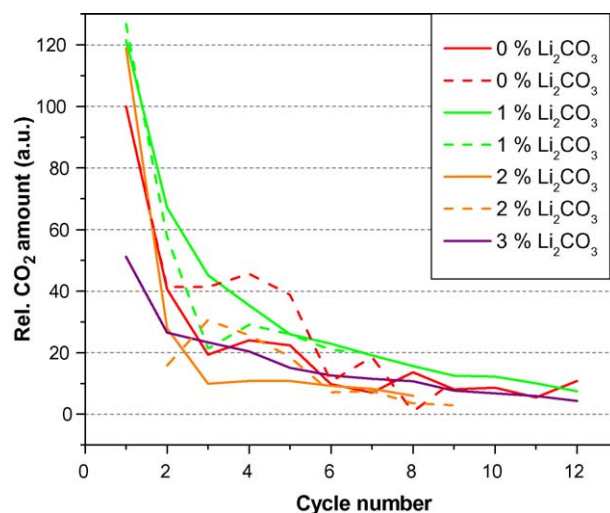


Fig. 3. Comparison of the amount of CO<sub>2</sub> evolved in cells with LNCAO cathodes and EC/PC/DMC, LiPF<sub>6</sub> at 60 °C, with various amounts of Li<sub>2</sub>CO<sub>3</sub> added to the cathode.

the initial cycles is enhanced compared to cells without added carbonate. Nevertheless, the amount of gas generated decreases quickly in the subsequent cycles, reaching a quite similar value in all experiments regardless of the amount of added carbonate. The curve for the electrode with 3% of added Li<sub>2</sub>CO<sub>3</sub> shows, in contrast to the other experiments, a reduced CO<sub>2</sub> evolution in the first cycle. So far we do not have a satisfying explanation of this behavior at 60 °C. Previous experiments at room temperature, both with the improved and the previously used DEMS measurement cell, did show an increased CO<sub>2</sub> evolution upon addition of 3% of carbonate.

### 3.4. Effect of vinylene carbonate

Vinylene carbonate (VC) is a well-known electrolyte additive for lithium-ion batteries, increasing the cyclability and reducing the irreversible capacity [8]. Although it is reactive on both electrodes, the positive effects of this additive are mainly attributed to reactions at the negative electrode [9]. In this study, we investigated the influence of VC on the CO<sub>2</sub> evolution at elevated temperature. Comparative measurements in cells with LNCAO with 3% of added Li<sub>2</sub>CO<sub>3</sub> and the EC/PC/DMC, LiPF<sub>6</sub> electrolyte, with and without addition of 2% of vinylene carbonate were performed (Fig. 4). In the presence of VC, the onset voltage of CO<sub>2</sub> formation is lower than in absence of the additive, but the total amount of CO<sub>2</sub> formed during the first cycle is much smaller. By integrating the area under the curves and normalizing this value by the positive active mass, the decrease of CO<sub>2</sub> evolution by addition of 2% VC is calculated to a factor of ca. 3.3. The same factor (ca. 3.3) was found in preliminary experiments at room temperature when cycling up to 5.1 V.

### 3.5. Improvement of the method

Due to drifting of the mass spectrometer signal over longer periods of time and various other influences, the DEMS measurements presented above are only comparable if they are



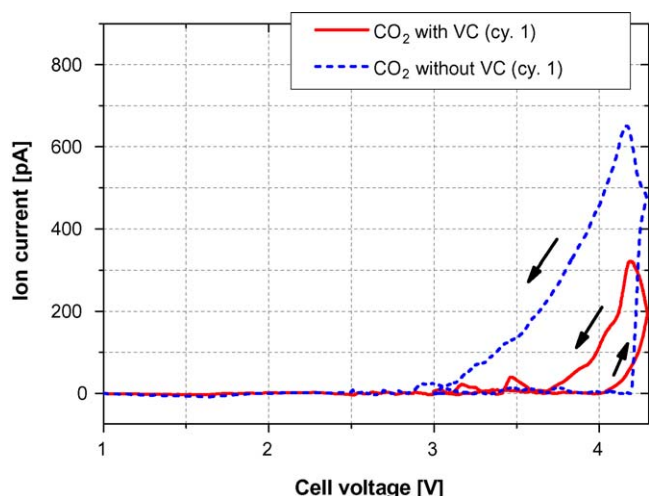


Fig. 4. CO<sub>2</sub> evolution in cells with LNCAO+3% Li<sub>2</sub>CO<sub>3</sub> cathodes and EC/PC/DMC, LiPF<sub>6</sub> electrolyte at 60 °C, without VC, and with 2% VC added to the electrolyte.

performed within a relatively small period of time of only a few weeks. In order to achieve a better comparability, the measurement setup had to be further improved. The final goal of establishing a fully quantitative method could not yet be reached, but nevertheless a significant improvement was achieved by introduction of a mass flow controller in the setup. Furthermore, due to the relatively high vapour pressure of the electrolyte at 60 °C, evaporation of volatile electrolyte compounds and condensation in the system was a severe problem, especially for longer-term measurements. In order to overcome these issues, the argon flown through the cell was saturated by passing it through a bubbler containing the volatile electrolyte components at the same temperature as the DEMS cell, and a condensation of electrolyte compounds between the cell and the mass spectrometer was added. A scheme of the setup is given in Fig. 5. Not only allows this setup prolonged measurements without loss of electrolyte, but also the signal-to-background ratio was greatly improved. While hitherto a manual baseline correction had to be done, the new setup renders a baseline correction unnecessary for the qualitative analysis of the raw data, eliminating a possible source of errors. This, together with the improved long-term sta-

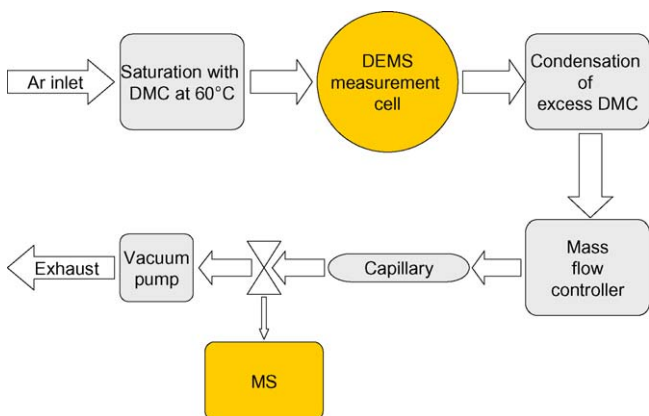


Fig. 5. Schematic drawing of the improved DEMS measurement setup.

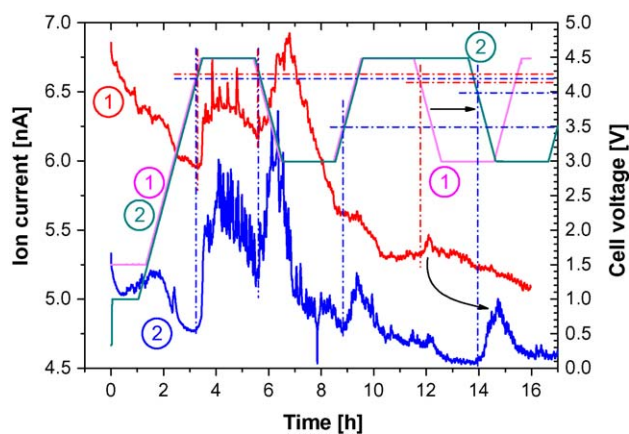


Fig. 6. CO<sub>2</sub> evolution in cells with LNCAO cathodes and EC/PC/DMC, LiPF<sub>6</sub> electrolyte at 60 °C. CV cycling with potentiostatic hold period at upper and lower voltage limit.

bility, allows reliable measurements that include a hold period at the voltage limits.

### 3.6. Mechanism and kinetics

Changes in the gas evolution during the hold period allow conclusions on the kinetics of CO<sub>2</sub> formation, an important parameter for the development of new battery materials with lower gas formation during storage and, thus, improved calendar life. In Fig. 6, the CO<sub>2</sub> evolution of two different cells with LNCAO positive electrodes in an experiment with potential hold at 4.5 V and at 3.0 V is shown. The curves are not baseline corrected. Despite of a slightly different background, the two curves are quite similar, showing the reproducibility of the method. During the first charge, a sharp increase of the CO<sub>2</sub> signal is observed at a cell voltage of ca. 4.2–4.3 V. The CO<sub>2</sub> evolution reaches a maximum shortly after the upper voltage limit (4.5 V) is reached and then decays slowly during the 2 h hold period. In the following discharge, the CO<sub>2</sub> signal again increases at a voltage of ca. 4.3–4.2 V, indicating the beginning of a second process releasing the gas. This second process dies away much more quickly than the first one. During the second charge, the raise of the CO<sub>2</sub> signal occurs at a much lower cell voltage of ca. 3.5 V, but the intensity and the amount of gas formed is much smaller. This can again be explained either by the consumption of a(n) (trace) impurity, or the formation of a passivating protective layer. During the second discharge, similar to the first cycle a CO<sub>2</sub> signal is observed. This signal appears at ca. 4.1 V in the first measurement and at ca. 3.5 V in the second one. In the second measurement, the hold period at 4.5 V in the second cycle has been extended to 4 h, resulting in a shift of the gas signal in time, indicated by arrows in Fig. 6. This shows that the CO<sub>2</sub> evolution is really associated with an electrochemical process during the lowering of the cell voltage. The most probable explanation seems to be the formation of a film or precipitate on the surface of the electrode or active material at high voltage above 4.3 V, and the dissolution of this compound at lower voltages, accompanied by the formation of CO<sub>2</sub>.

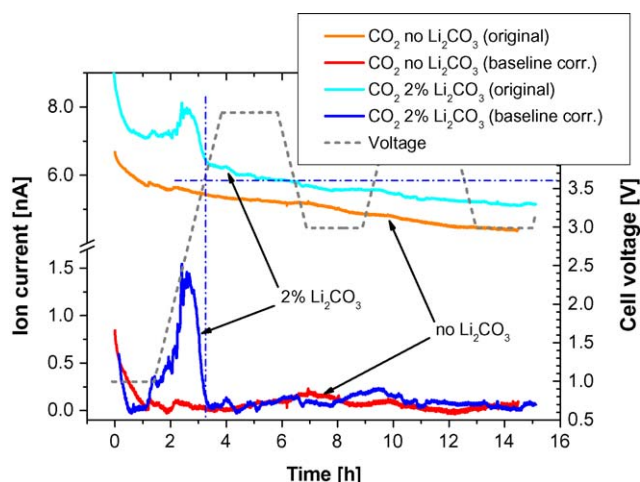


Fig. 7. CO<sub>2</sub> evolution in cells with LNMCO cathodes with and without added Li<sub>2</sub>CO<sub>3</sub> and EC/PC/DMC, LiPF<sub>6</sub> electrolyte at 60 °C, with potentiostatic hold period at upper and lower voltage limit. Original and baseline corrected DEMS curves.

### 3.7. Lithium nickel manganese cobalt oxide

As a second positive active material, Li(Ni, Mn, Co)O<sub>2</sub> (LNMCO) was tested on its CO<sub>2</sub> evolution in dependence of the cell voltage. Our experiments showed only a very small amount of CO<sub>2</sub> evolved from these electrodes at 60 °C. In fact, the signals detected could hardly be distinguished from the noise and did not allow a reliable correlation with the cell voltage (Fig. 7). Since the material contains only very small amounts of Li<sub>2</sub>CO<sub>3</sub>, we were wondering if this could be the crucial parameter for CO<sub>2</sub> evolution. We therefore added 2% of lithium carbonate to the electrode and monitored the gassing behavior of this intentionally contaminated electrode. Surprisingly, a strong CO<sub>2</sub> signal is observed at very low cell voltages, but gas evolution stops at ca. 3.5–3.8 V in the first charge. Neither during the hold period at 4.5 V, nor in the subsequent cycles, any influence of the added lithium carbonate on CO<sub>2</sub> formation is observed (Fig. 7). This is a strong hint that inorganic carbonate present in the LNMCO has only a minor impact on the evolution of CO<sub>2</sub> at high voltages and elevated temperatures.

## 4. Conclusions

In cells comprising LNCAO cathodes and EC/PC/DMC, LiPF<sub>6</sub> electrolyte, high cell voltages and high temperatures promote the formation of CO<sub>2</sub>. At elevated temperature, the onset

voltage of gas evolution is shifted to lower voltages. Upon prolonged cycling, the amount of CO<sub>2</sub> evolved decreases, indicating either the consumption of a (trace) compound or impurity, or the formation of a passivating protective layer. If 1–2% of lithium carbonate is added to the positive electrode, the amount of CO<sub>2</sub> evolved in the initial cycles is increased, but the effect seems to be of minor importance during prolonged cycling. Nevertheless, the addition of 3% Li<sub>2</sub>CO<sub>3</sub> seems to reduce the gas evolution at 60 °C, possibly due to a different process. In the presence of vinylene carbonate in the electrolyte, the CO<sub>2</sub> evolution is reduced. CO<sub>2</sub> evolution in LNCAO cells occurs in two steps. At 60 °C and cell voltages of ca. 4.2–4.3 V a first process releasing CO<sub>2</sub> starts in the first CV cycle, continuing for more than 2 h if the cell voltage is held at 4.5 V. During discharge in the first cycle, a second process occurs at ca. 4.3–4.2 V, but the CO<sub>2</sub> evolution fades away much more quickly. During the second cycle, similar processes are observed, but the onset voltages are shifted to lower voltages, and the amount of CO<sub>2</sub> generated is smaller. Only very small amounts of CO<sub>2</sub> seem to be generated at LNMCO electrodes at 60 °C. Addition of 2% Li<sub>2</sub>CO<sub>3</sub> to LNMCO results in CO<sub>2</sub> evolution at low voltages (> ca. 3.8 V), but doesn't affect the gassing behavior during subsequent cycling.

## Acknowledgements

Financial support by the European Community and the Swiss State Secretariat for Education and Research (contract no. 02.0004-1) under the framework of the European research project CAMELiA (ENK6-CT-2002-00636) is gratefully acknowledged.

## References

- [1] K.H. Lee, E.H. Song, J.Y. Lee, B.H. Jung, H.S. Lim, J. Power Sources 132 (1–2) (2004) 201–205.
- [2] N. Takami, T. Ohsaki, H. Hasebe, M. Yamamoto, J. Electrochem. Soc. 149 (1) (2002) A9–A12.
- [3] R. Imhof, P. Novak, J. Electrochem. Soc. 146 (5) (1999) 1702–1706.
- [4] P. Novak, J.C. Panitz, F. Joho, M. Lanz, R. Imhof, M. Coluccia, J. Power Sources 90 (1) (2000) 52–58.
- [5] A. Wuersig, J. Ufheil, P. Novák, 205th ECS Meeting, San Antonio, TX, USA, May 9–13, 2004, no. 78.
- [6] P. Novak, D. Goers, L. Hardwick, M. Holzappel, W. Scheifele, J. Ufheil, A. Wuersig, J. Power Sources 146 (1–2) (2005) 15–20.
- [7] A. Wuersig, PhD thesis no. 16059, ETH Zurich, 2005.
- [8] B. Simon, J.P. Boeue, EP 5,626,981 (1997).
- [9] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, Electrochim. Acta 47 (9) (2002) 1423–1439.