

# Metallic lithium batteries for high power applications

I. Stassen\*, G. Hambitzer

FORTU® BAT Batterien GmbH, Wöschbacher Strasse 37, D-76327 Pfinztal, Germany

## Abstract

This paper presents a new inorganic rechargeable battery system with  $\text{LiCoO}_2$  as the positive electrode of the battery whereas metallic lithium is plated onto the negative current collector. The electrolyte is based on  $\text{LiAlCl}_4$  and  $\text{SO}_2$ . The inorganic character of the battery results in a new principle of operation which affords only a limited amount of metallic lithium in the cell. The positive intercalation electrode determines the amount of lithium in the cell in its charged state. Compared to other metallic lithium battery systems, no surplus of lithium is needed. This leads to a safe and reliable accumulator with excellent performing characteristics for electric vehicle and cordless tools applications. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Inorganic rechargeable lithium battery; Electric vehicle application; Cordless tool application

## 1. Introduction

Since the mid-seventies primary metallic lithium batteries have been established for high energy applications due to the ability of delivering electric energy for a long operating time at low power requirements. Several types of cells are utilized, for example, in watches, hearing aids, pace makers and batteries for military purposes. The rapidly growing demand for an improved battery performance, e.g. a higher storable energy at a lower weight and volume as well as an increased power density has led to a great variety of new developments, especially in the field of rechargeable metallic lithium batteries. Lithium is the most lightweight metal with the highest electrochemical potential and therefore, suitable for high energy and high power applications as illustrated now for the case of this new inorganic rechargeable metallic lithium battery.

## 2. Experimental

The cells contain mainly inorganic components. The cathode material is  $\text{LiCoO}_2$ , as is known from the lithium ion technology. But, in contrast to the former, no carbon intercalation electrode is needed on the negative side but pure metallic lithium is plated on to a nickel substrate leading to a theoretical specific energy of 1070 Wh/kg. The electrolyte

solution is based on the solvate of  $\text{LiAlCl}_4$  and  $\text{SO}_2$  which results, at room temperature, in a clear liquid with a conductivity of more than 20 mS/cm. The vapor pressure of  $\text{SO}_2$  at room temperature is approximately 20 mbar which increases at 70 °C to 1 bar. All components are chemically inert in respect to the electrolyte solution, in particular lithium forms a protecting, ion-conducting surface layer [1].

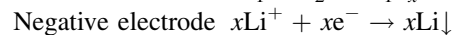
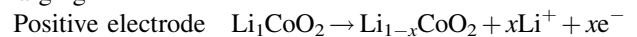
The cells are assembled in their discharged condition without the necessity to handle any metallic lithium in the production process.

## 3. Results

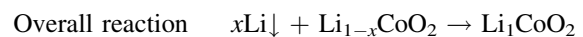
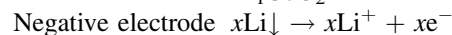
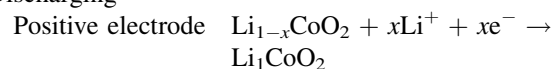
### 3.1. Cell chemistry

The fundamental cell reactions are as following:

#### Charging



#### Discharging



During charging lithium ions are deintercalated out of the  $\text{LiCoO}_2$  lattice and are deposited on the negative electrode as

\* Corresponding author. Tel.: +49-721-94668-19;

fax: +49-721-94668-88.

E-mail address: i.stassen@fortu.de (I. Stassen).

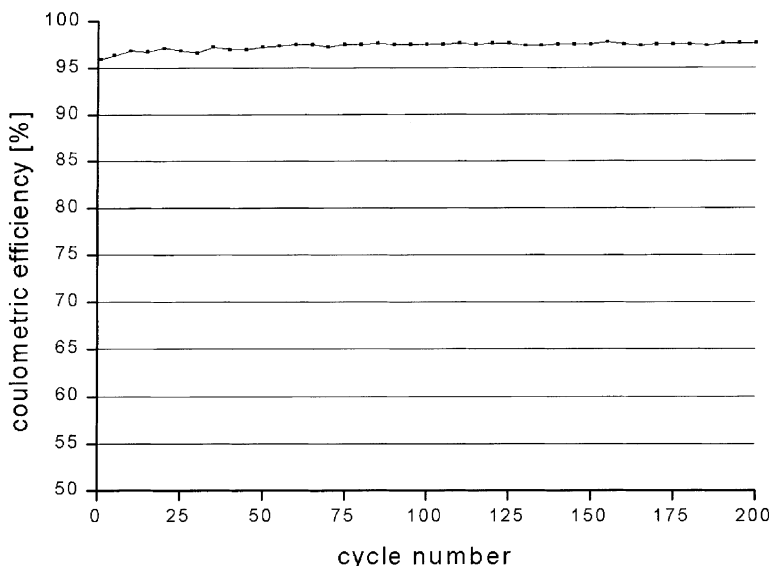


Fig. 1. Coulometric efficiency of lithium cycling in inorganic electrolyte current density 8 mA/cm<sup>2</sup>, electrode area 0.64 cm<sup>2</sup>.

metallic lithium, protected by a surface layer consisting of Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub> [1,2]. The surface layer is formed by reaction of lithium with the solvent SO<sub>2</sub> of the inorganic electrolyte. Fig. 1 shows the coulometric efficiency of the lithium plating and dissolution in inorganic electrolyte solution as a function of the cycle number. The measurements were performed on a nickel plate at a current density of 8 mA/cm<sup>2</sup> both for plating and dissolution of lithium.

### 3.2. Overcharge and self-discharge mechanisms

#### Overcharge reaction

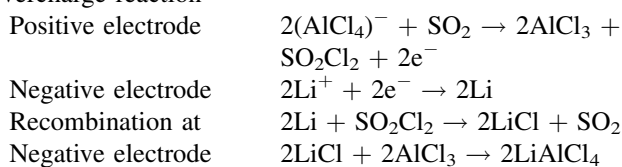
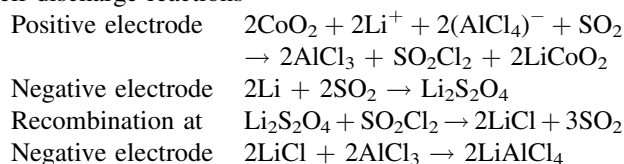


Fig. 2 shows a cyclic voltammogram of LiCoO<sub>2</sub> in inorganic electrolyte solution at a scan rate of 0.2 mV/s. The anodic peaks at 4, 4.1 and 4.2 V versus Li represent the deintercalation of lithium ions out of the cobalt dioxide lattice with the corresponding cathodic intercalation peaks occurring during discharging of the electrode. At a potential of 4.4 V, the beginning of the overcharging process is observed. While overcharging decomposition of the anion of the conducting salt (AlCl<sub>4</sub>)<sup>-</sup> is observed at the positive electrode yielding aluminium trichloride and suluryl chloride as products [2–4]. Liquid suluryl chloride is formed directly at the electrode which readily dissolves in the electrolyte solution and therefore easily diffuses to the negative electrode where lithium is still deposited. Suluryl chloride oxidizes the lithium dithionite surface layer and

delivers lithium chloride and sulfur dioxide. This reaction is indicated by warming of the cell. Further on lithium chloride and aluminium trichloride which have been formed at the positive electrode recombine and lead back to lithium tetrachloroaluminate. So, the overall reaction is a closed circuit which represents a real overcharge mechanism. Therefore, no costly external electronic charge control is necessary as is known in the case of e.g. lithium ion cells.

#### Self-discharge reactions



The self-discharge process is similar to the overcharge mechanism. Again, suluryl chloride is the product of the self-discharge reaction at the positive electrode [2]. The dissolution of metallic lithium by sulfur dioxide and the subsequent formation of the lithium dithionite surface layer represents the self-discharge mechanism of the negative electrode. The thickness of the surface layer reaches a constant value which is determined by the diffusion-limited migration of sulfur dioxide through lithium dithionite [1,5]. When suluryl chloride, which is formed at the positive electrode, reaches the negative electrode and reacts with lithium dithionite the same products are generated as in the case of the overcharge mechanism. Here again, all reaction partners are transferred back to components of the electrolyte solution. The overall process is determined by the positive mass and the development of suluryl chloride.

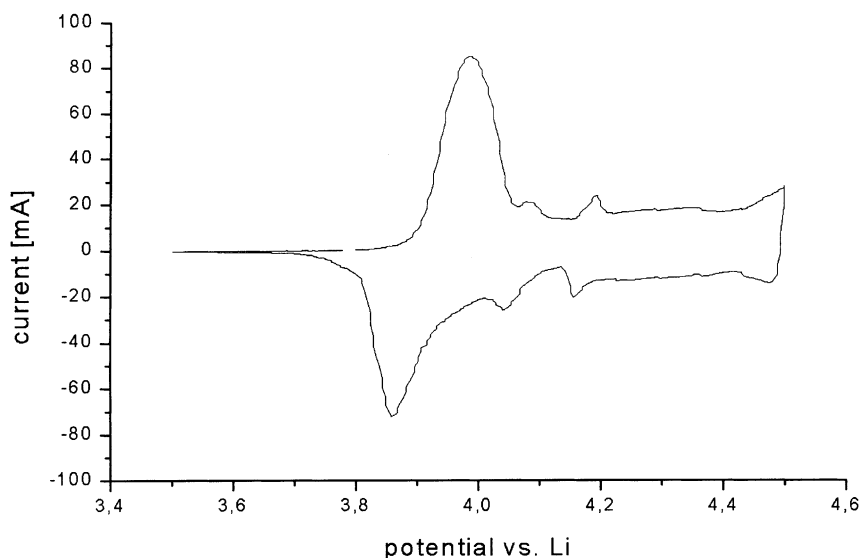


Fig. 2. Cyclic voltammogram of  $\text{LiCoO}_2$  in inorganic electrolyte solution; electrode area,  $2 \text{ cm}^2$ ; scan rate,  $0.2 \text{ mV/s}$ ;  $3.5\text{--}4.5 \text{ V}$  vs. lithium.

In this inorganic system both the overcharge and the self-discharge process deliver only a limited amount of possible reactions with only very few reactions partner. This leads to a new principle of operation with no surplus of lithium needed in the cell. The amount of lithium in the cell is set by the capacity of the positive electrode.

### 3.3. Cycle life

The usual charging procedure is a constant current charging procedure until 55% of the theoretical capacity is reached. The nominal capacity of the cell is 50% of the theoretical capacity. Both charge and discharge rate are  $1 \text{ C}$  with four cycles per day. According to this procedure up to now a cycle life of 350 cycles until 80% of the nominal capacity has been achieved. Since the cathode material is

$\text{LiCoO}_2$  as in lithium ion technology further improvement of the cycle life is expected with ongoing optimization.

### 3.4. Cycling of large cells

The cells had the dimensions of  $158 \text{ mm} \times 114 \text{ mm} \times 33 \text{ mm}$ . The electrodes were stacked and inserted into the prismatic stainless steel housing. The finally mounted cells have a nominal voltage of  $4 \text{ V}$  at a capacity of nearly  $50 \text{ Ah}$  and a weight of  $1.2 \text{ kg}$ . So, in this non-optimized construction a specific energy of  $160 \text{ Wh/kg}$  has been achieved. Fig. 3 shows two full charge/discharge cycles which were performed in constant current mode. Charging was ended when the capacity reached  $50 \text{ Ah}$  and discharge was stopped when the cut-off voltage dropped below  $2.5 \text{ V}$ . Cycling efficiency was 97%.

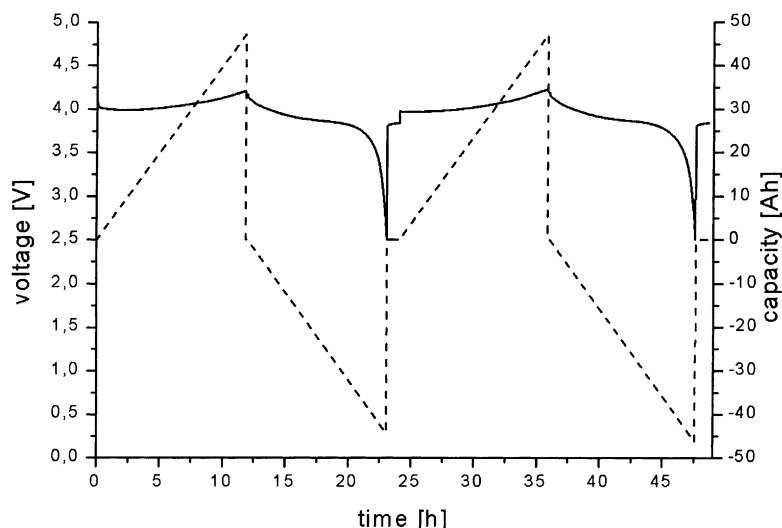


Fig. 3. Charge/discharge curves of a  $50 \text{ Ah}$  cell.

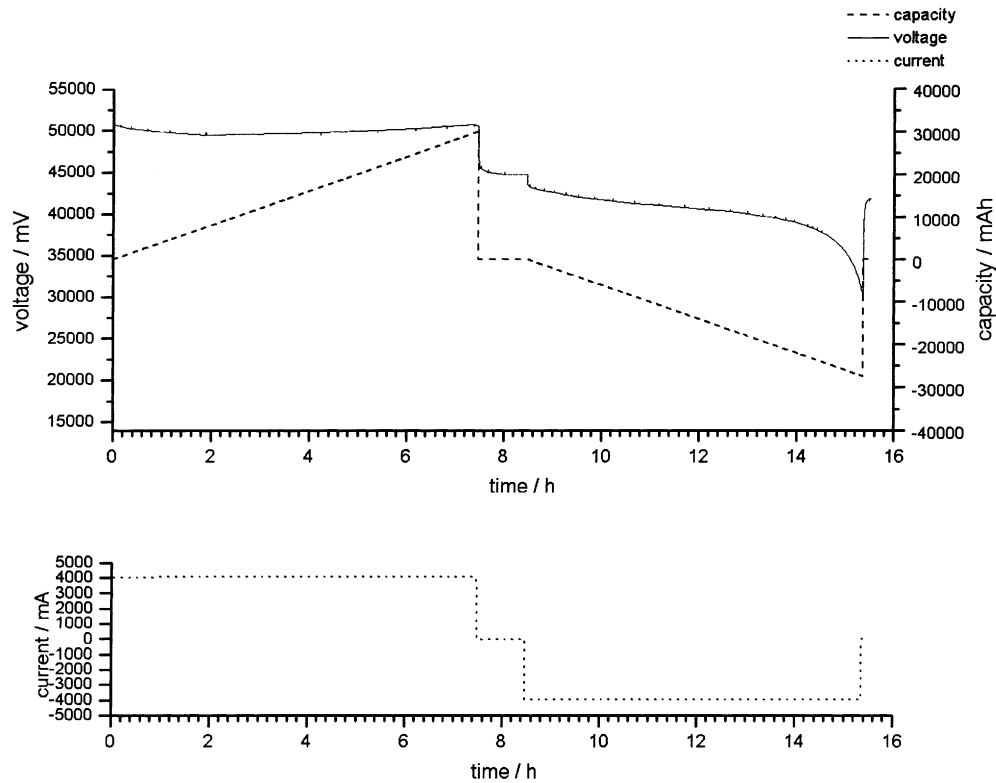


Fig. 4. Charge/discharge curves of a 48 V/30 Ah battery.

### 3.5. Cycling of modules

In order to demonstrate the ability of the cell for series connection a 48 V/30 Ah module has been built. This means that two modules were connected in series, each module comprising six cells with a capacity of 30 Ah. The battery management provides one single voltage and temperature control of a six cell (24 V) module. Due to the overcharge mechanism of the battery system the costly electronic monitoring of each single cell is unnecessary. The end of charging is indicated when the overall cut-off voltage of the module is reached or when a certain temperature increase is observed.

Fig. 4 illustrates the charge/discharge curve of a 48 V/30 Ah battery. There is no significant difference in the corresponding curve of the single cell presented in the previous section. The cycling efficiency was 92%.

One possible application of the inorganic lithium metal cells is in the field of electric vehicles. In order to demonstrate the capability of the cells as an energy storage device in electric vehicles a load profile was applied to a module according to the New European Drive Cycle (NEDC). Vehicles are most commonly tested with the NEDC. The NEDC consists of four consecutive city drives with a maximum velocity of 50 km/h and a final high speed drive with 120 km/h. When taking into account the weight of an electric car, its flow and frictional resistance etc, the corresponding velocity profile can be transferred into a load

profile with variable discharge rates for the electric vehicle battery. And the NEDC provides regenerative braking so that that the battery is charged when the car slows down.

Fig. 5 shows the charge/discharge curves of a 24 V/3 Ah module. The left cycle illustrates first the charging of the module and then a variable discharge according to the NEDC. A voltage drop is observed when the cells are discharged at different rates and a voltage increase occurs when the cells are charged by regenerative braking. The NEDC was passed through several times before the discharge was stopped by a constant current until the voltage dropped below the cut-off limit. After this cycle with varying discharge rates a constant current cycle followed as illustrated in the right part of Fig. 5. When these two cycles are compared no significant difference concerning the coulometric and energy efficiency is noticeable which are 90 and 85%, respectively. Further improvement of these data is expected when a large scale production allows a better matching of the cells.

### 3.6. High power cells

Up to now the focus of the development was put on high energy cells but first experiments have been conducted which demonstrate the high power capability of the battery system.

The cells were mounted in a stainless steel housing with the dimensions of 76 mm × 52 mm × 14 mm. A single

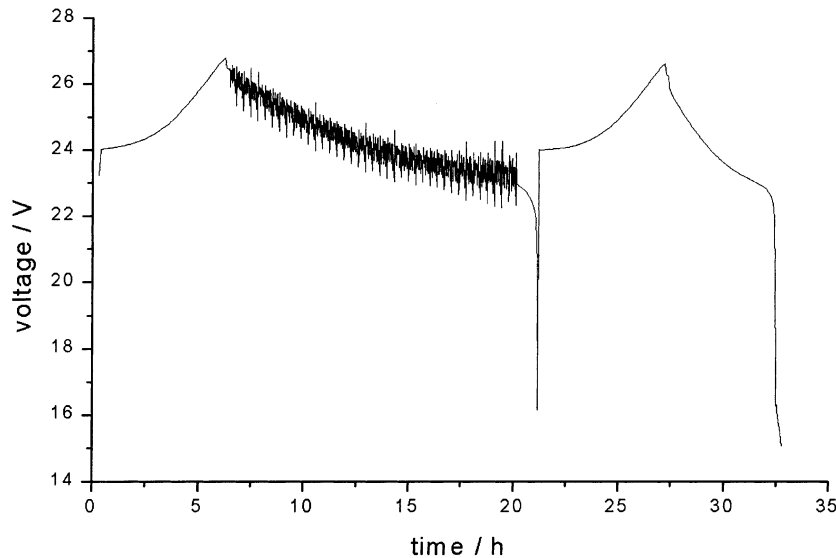


Fig. 5. Charge/discharge curves of a 24 V/3 Ah module according to a NEDC.

positive electrode and two negative electrodes were stacked with a spacer filling the void volume. These cells were discharged at a 16 C rate. Based on the results, obtained with the non-optimized cells, the specific power was calculated to be 1400 W/kg, still at a specific energy of 80 Wh/kg. At a specific power of 100 W/kg a specific energy of 160 Wh/kg is obtainable.

### 3.7. Safety

The safety of metallic lithium batteries is still a matter of controversy. So, safety testing has been performed extensively with the cells. Various fresh cell with different capacities up to 50 Ah have been built and subjected to nailing, heating and short-circuiting.

Nailing of a 3 Ah cell yielded a temperature increase, measured at the housing, of a maximum of 160 °C. the same test with 50 Ah cell resulted in a maximum temperature 200 °C. The ejection of material in all cases was very limited, with sulfur dioxide out of the electrolyte being the main substance to arise. The results are summarized in Table 1. Heating and short-circuiting delivered similar results. In no case was any serious event observed. Currently, the same experiments are being carried out with cycled cells. Preliminary results show no decrease in safety performance due to the fact that no surplus of lithium is necessary in the cell.

Table 1  
Safety features of the inorganic lithium metal cells

Criteria	Inorganic lithium metal (0.5–50 Ah)
Ejection of material (g/Ah)	0–2
Temperature increase (K)	150–200

## 4. Conclusion

Because of the metallic lithium anode very high energy and power densities have been achieved. Designed as a high energy battery, specific energies of 200 Wh/kg are obtainable. The current state-of-the-art is a 4 V/50 Ah cell with 160 Wh/kg. Further improvements in electrode design, manufacturing and stacking as well as a optimization in cell fabrication will lead to higher energy densities. The aim is a 4 V/65 Ah cell and respectively a 24 V/65 Ah module with both having a specific energy of at least 200 Wh/kg which is very reasonable when keeping in mind that the thermodynamic energy density is as high as 1070 Wh/kg. Thus this battery system is a suitable candidate for e.g. electric vehicles or other automotive application.

When the cell is optimized towards high power applications a specific power of 1400 W/kg is attainable. The specific energy at this power output is 80 Wh/kg. Charging of the full cell capacity is completed within 1 h. So the use of this cells in power tools or cordless tools is feasible.

The safety of the cells has been extensively tested by heating, nailing and short circuiting. No fire or flames have been observed in any of the abuse tests mentioned and the loss of cell material has been very limited. Due to the new principle of operation no surplus of lithium exists in the cells and therefore no difference between fresh and cycled cells has been observed in all safety experiments.

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