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Purification process for an inorganic rechargeable lithium battery and new safety concepts

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Abstract

We have investigated an inorganic lithium battery system in which $LiCoO_2$ is used as the positive electrode and lithium, intercalated into graphite, serves as negative electrode. The conducting salt is lithium tetrachloroaluminate ($LiAlCl_4$). The electrolyte is based on SO_2. It has been shown that a layer of lithium hydroxide is present on the surface of the lithium cobalt oxide. This has a negative impact on the stability of the electrode. To improve stability, we have developed a purification process for removing the lithium hydroxide from the surface of the positive electrode. After purification the cells show no significant change in either capacity or internal resistance when cycled. Up to 70% of the theoretical capacity of electrodes which have been purified in this way can be used without any negative effects being observed. To prevent the deposition of metallic lithium leading to a hazardous situation, a new safety concept was developed whereby local short circuits are allowable. Safe functioning of the new concept has been demonstrated with tests on complete cells.

1. Introduction

The biggest issue with lithium-ion batteries is safety. Battery cells normally have a separator, which allows no electrical current flow between the electrodes. The separator in a lithium-ion-accumulator also should prevent short circuits between the negative and the positive electrodes due to dendritic growth of metallic lithium. This can happen with lithium-ion- or lithium-polymer-cells, for example, if the cell is overcharged or at the end of the charging phase with a cell which has been subject to many charge/discharge cycles [1].

If there is a separator failure and short circuits occur, the safety risk with a lithium-ion cell is large. The rapid increase in temperature caused by short circuits may lead to safety-critical conditions. The cell housing may leak and harmful gaseous substances be released. If the housing ruptures, gaseous and solid substances may escape. There is also a danger of fire or, in extreme cases, explosion [2–4].

It is not only internal short circuits which can cause a temperature increase. Improper handling or external short circuits can lead to destruction of the cell, especially if metallic lithium is present.

Battery manufactures attempt to prevent thermal runaway by controlling the charging and/or discharging process. By using electronic protection circuits and mechanical or chemical protections such as shut down separators, the flow of electrical current is interrupted before critical temperature or voltage conditions arise.

The goal of this work is to design a lithium cell with a level of high safety but without degradation of the otherwise good electrical properties.

To avoid critical conditions we have developed a rechargeable lithium battery based on a new and unique safety concept. The cell needs no complicated charge/discharge control mechanisms, because there are no safety risks which can arise during cycling, overcharging or deep discharging. Stable cell behaviour is ensured by a new system based on an inorganic electrolyte.

To get better electrical properties we have developed a purification method for the components of the battery cell. The system also allows a higher deintercalation state of the positive electrode to be reached than is possible with standard lithium-ion cells.

2. Experimental details

2.1. *Cell materials and reactions*

$LiCoO_2$ is used as the positive electrode of the battery whereas lithium, intercalated into graphite, serves as negative electrode. The conductive salt is lithium tetrachloroaluminate $LiAlCl_4$. The electrolyte contains SO_2 in a low concentration, for example $LiAlCl_4 \times 1{,}5SO_2$. The high mobility of ions of the conductive salt, which is contained in the electrolyte and is responsible for the charge transport, is at least in part due to the SO_2 [5]. SO_2 has good ionic transport properties because it has a very high dielectric constant of 17. The electrolyte has a good conductivity of $70\ mS\ cm^{-1}$ at room temperature. So the electrolyte resistance is very small. Because the electrolyte contains only inorganic components, there are not many side reactions, which decompose the electrolyte [6].

While overcharging decomposition of the anion of the conducting salt $(AlCl_4)^-$ is observed at the positive electrode yielding aluminium trichloride and sulfuryl chloride as products. Liquid sulfuryl 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. Sulfuryl 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.

Overcharge reaction	
Positive electrode	$2(AlCl_4)^- + SO_2 \rightarrow 2AlCl_3 + SO_2Cl_2 + 2e^-$
Negative electrode	$2Li^+ + 2e^- \rightarrow 2Li$
Recombination at	$2Li + SO_2Cl_2 \rightarrow 2LiCl + SO_2$
Negative electrode	$2LiCl + 2AlCl_3 \rightarrow 2LiAlCl_4$

Charging the battery causes lithium ions to move out of the cobalt oxide lattice and slip between sheets of carbon atoms in the graphite electrode. Discharging the battery causes the ions to move back again, releasing energy in the process. The fundamental cell reactions are as follows:

Charging	
Positive electrode	$Li_1CoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$
Negative electrode	$xLi^+ + xe^- + C_6 \rightarrow xLiC_6$
Overall reaction	$Li_1CoO_2 \rightarrow Li_{1-x}CoO_2 + xLiC_6$
Discharging	
Positive electrode	$Li_{1-x}CoO_2 + xLi^+ + xe^- \rightarrow Li_1CoO_2$
Negative electrode	$xLiC_6 \rightarrow xLi^+ + xe^- + C_6$
Overall reaction	$Li_{1-x}CoO_2 + xLiC_6 \rightarrow Li_1CoO_2$

2.2. *Safety concept*

The capacity of lithium ion cells is generally limited by the positive electrode. This means that the capacity of the negative electrode is chosen so that the total quantity of lithium transferred during charging can definitely be stored. The capacity of the positive electrode falls as the cell is cycled, which means that it remains the capacity-limiting factor throughout the complete life of the battery. When overcharged, however, metallic lithium will be deposited onto the surface of the negative electrode, which in turn can lead to safety-critical situations including fire or explosion.

Our inorganic system is also capacity-limited by the positive electrode. The overcharge reaction, however, ensures that no metallic lithium is deposited on the negative electrode, neither when overcharged nor when cycling [7, 8]. But even if the cell were capacity-limited by the negative electrode, the overcharge mechanism precludes any critical safety situations from arising.

If a negative-electrode limited cell is overcharged, very small whiskers of pure lithium are formed on the surface of the graphite [9, 10]. The whiskers grow directly to the positive electrode. If too much lithium accumulates and then contacts the positive electrode, the resulting short circuit could cause thermal runaway. We have found that limiting the short circuits to local areas prevents accumulation and eliminates the risk of a runaway condition.

If short circuits caused by whiskers are spatially separated, the resulting behaviour of the cell is very different from that expected of lithium systems. The reactions neither lead to thermal runaway, nor to destruction of the electrodes or electrolyte. There are no irreversible reactions which cause a reduction of cell capacity, although very high current densities of up to 5C were measured.

The growth of the whisker correlates to the net charging current. A whisker hitting the surface of the positive electrode leads to a pulse discharge current and to the dissolution of the whisker. Depending on the resulting current all other whiskers stop to grow further. Heat production during overcharge and the thickness of the whisker depend on net overcharge current density.

During short circuits caused by whiskers, lithium reacts to lithium-ions in a normal discharge reaction:

$$xLi + Li_{1-x}CoO_2 \rightarrow LiCoO_2 \tag{5}$$

To allow local short circuits, the cell has no nanoporous separator preventing a contact between lithium and the positive electrode. Instead of a conventional separator, a porous isolator is used. The pores of the isolator must be big enough to allow whiskers to penetrate it, but prevents direct electrical contact between the negative and positive electrodes. With this design it is possible that the active mass of lithium, deposited on the surface of the negative electrode, contacts the positive electrode at local points. The metal grows through the pores of the isolator until the positive electrode is reached.

3. Results and discussion

3.1. *Purification of the positive electrode*

Lithium cobalt dioxide $(LiCoO_2)$, in its delivered state, has a thin layer of lithium hydroxide (LiOH) on the surface. We assume that freshly manufactured lithium cobalt oxide is highly hygroscopic and reacts with water in the following way:

$$LiCoO_2 + xH_2O \rightarrow xLiOH + Li_{1-x}H_xCoO_2 \qquad (5)$$

Thus, lithium ions from the lithium cobalt oxide are replaced by protons. For material with a grain size of 5 μm, the proportion of lithium ions in the lithium cobalt lattice replaced by protons is approximately 5%.

We have developed a purification solution to remove lithium hydroxide from the electrode. This solution contains a Lewis acid which reacts with the lithium hydroxide [11]. Following removal of the purification solution and impurities dissolved during the process, the electrodes are ready for operation in the cell. The purification leads to a much better cycle stability and a higher capacity.

While cycling positive electrodes with a capacity of 41 mAh cm^{-1} and a thickness of 0.6 mm in a potential range 3.5–4.5 V the measured capacity without purification is 58% of the theoretical capacity. If the electrodes are purified the capacity increases to 71% of the theoretical capacity, because all Hydrogen-ions are replaced with Li-ions.

Figure 1a and b show 40 cycles of a cyclic voltammogram of contaminated (1a) and purified (1b) $LiCoO_2$-electrodes. The cyclic voltammetry experiments comprise a three electrode system (working electrode: $LiCoO_2$, counter electrode: Li, reference electrode: Li) placed in a glass half cell (E-type) The voltammograms were recorded across the potential range from 3.5 V to 4.5 V with a sweep rate of 0.2 mV/ s^{-1}.

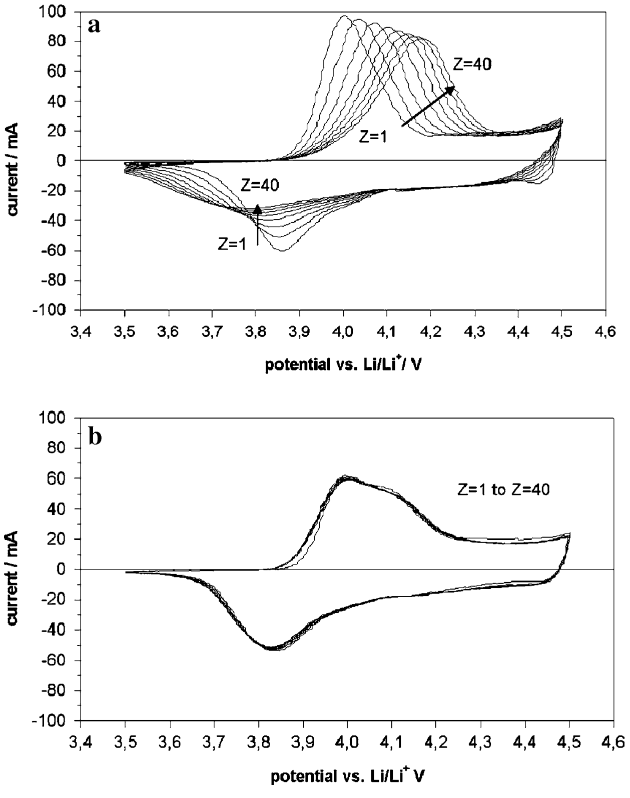

Fig. 1. (a)Cyclic voltammogram of contaminated $LiCoO_2$-electrodes (40 cycles). (b) Cyclic voltammogram of purified $LiCoO_2$-electrodes (40 cycles).

During cycling of the contaminated electrode, the peak-potential increases from 3.95 V to 4.20 V. This means the internal resistance is increasing. Figure 1b shows the cyclic voltammograms of a purified electrode. There is no drift of the peak voltage and no change in the internal resistance.

3.2. *Capacity of the positive electrode, deintercalation over 50%*

The specific energy of a system using Li/$LiCoO_2$ is 1100 Wh kg^{-1}. For a system using LiC_6/$LiCoO_2$, the specific energy is 580 Wh kg^{-1}. In lithium ion cells, typically 50% of the theoretical capacity of the $LiCoO_2$ is used. Conventional wisdom is that the lithium cobalt oxide lattice will be irreversibly damaged and capacity lost, if more than 50% of the lithium stored in the positive electrode is used [12].

We have shown that up to 70% of the lithium was deintercalated out of the lithium cobalt dioxide, without any negative impact, with our inorganic system using purified electrodes. Our measurements show that in spite of the higher charging level, the $LiCoO_2$ lattice is not destroyed. The capacity over many cycles is constant. Figure 2 shows 750 cycles measured with cyclic voltammetry.

3.3. *Cycling of cells*

Full cells with the following characteristics were built. Capacity was 1.3 Ah and the nominal voltage 3.8 V. The housing was 42 × 13.5 × 45 mm with a weight of 82 g and volume of 0.026 l. The cells were mounted in stainless steel housings. Nine positive $LiCoO_2$ electrodes and 10 negative graphite electrodes were stacked. Nickel foam was used as carrier material for both electrodes.

3.3.1. *High energy/high current characteristics*

The specific energy of the system described is up to 250 Wh kg^{-1} and the energy density can exceed 750 Wh l^{-1}. With cells designed for high power, it is

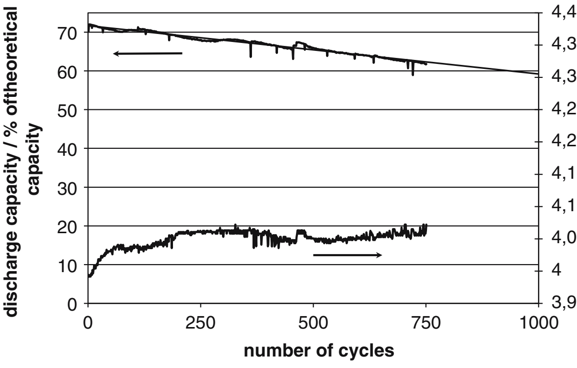

Fig. 2. Discharge capacity and peak potential of a $LiCoO_2$-electrode with a deintercalation state greater than 70% (about 750 cycles).

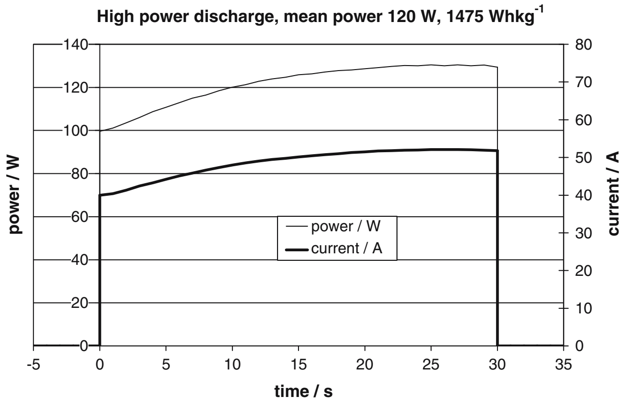

Fig. 3. Power and current of a 30 s high power discharge with a specific power of 1475 W kg^{-1}.

possible to achieve very high constant power levels. Figure 3 shows a 30 s high power discharge with a specific power of 1475 W kg^{-1}.

3.3.2. *Battery cell with purified electrodes*

Not does the $LiCoO_2$ electrode work better after purification, but other components including separator and negative electrode also benefit. With such electrodes it is possible to build a long life accumulator. Figure 4 shows the stability of capacity of a purified cell over 230 cycles.

The capacity loss in the first cycle depends on the building of the lithium dithionite surface layer on the electrode.

$$2Li + 2SO_2 \rightarrow Li_2S_2O_4 \tag{5}$$

In the following eight cycles the characteristics of the cell were identified. The end of charge was at a voltage of 4.1 V. After that for all other cycles the end of charge was defined at a voltage of 4.2 V.

3.3.3. *Deep discharge to cell voltage of 1.5 V*

To demonstrate the deep discharge characteristics of the cells, five test cycles were made (Figure 5, measured by ZSW). The charge and discharge current were both 1 A. The maximum charge voltage was 4.1 V. End of charge was defined as either 110% of nominal capacity or minimum current I_{min} = 130 mA. The end of discharge was a cell voltage of 1.5 V. The time interval between charge and discharge was 10 min and between discharge and charge 60 min. After five deep discharge cycles, no change in the behaviour of the cell was observed. No significant changes in capacity and internal resistance were detected.

3.3.4. *Overcharge characteristics*

To demonstrate the overcharge characteristics of the cell, one test cycle was made (Figure 6, measured by ZSW). The charge and discharge current were both 1 A. The charge voltage to reach the nominal capacity was 4.1 V. The end of charge was defined as the point where nominal capacity was reached. Then the cell was overcharged with a maximum current of 0.3 A and maximum charge voltage of 4.4 V until 200% of the nominal capacity was reached. After a pause of 10 min the cell was discharged to the discharge cut off voltage of 2.5 V.

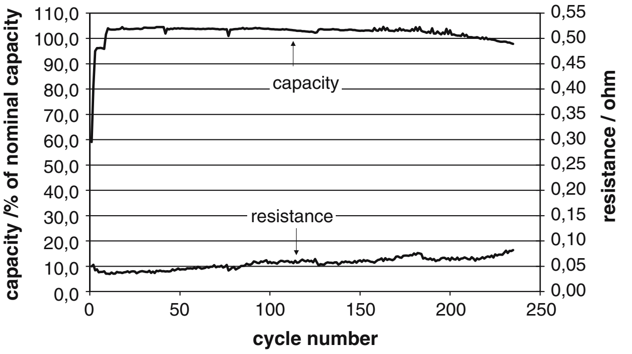

Fig. 4. Capacity and internal resistance of a purified battery cell (230 cycles).

After 100% overcharging the capacity increased up to nearly 150% (approximately 1850 mAh) of the value reached with the last 1 C cycle. The overcharge reaction (see 2.1.) would be responsible for the capacity loss of 50%.

4. Conclusions

A rechargeable inorganic battery cell where $LiCoO_2$ is used as the positive electrode and lithium, intercalated into graphite, serves as negative electrode was investigated. The electrolyte is based on SO_2 with lithium tetrachloroaluminate as conducting salt.

We found that commercially available $LiCoO_2$ has a layer of lithium hydroxide on the surface. A purification method was developed, whereby the lithium hydroxide was removed from the electrode using a special purification solution. The purification leads to improved cycle stability. After purification neither the peak potential nor the internal resistance increased significantly while cycling.

Using an inorganic electrolyte in combination with the purification process it is possible to create positive

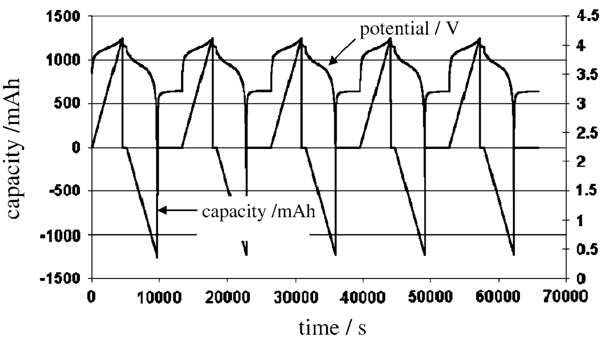

Fig. 5. Capacity and voltage of 5 deep discharge cycles to cell voltage of 1.5 V.

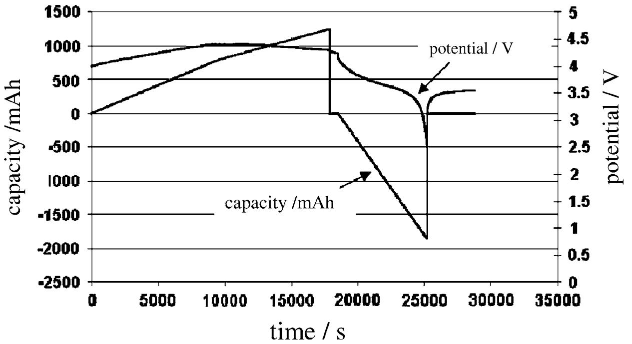

Fig. 6. Overcharge cycle of up to 200% of the nominal capacity.

electrodes where up to 70% of the lithium can be deintercalated out of the lithium cobalt dioxide without negative consequences. In spite of the higher charging level, the $LiCoO_2$-lattice was not destroyed and the usable capacity was still above 80% of the initial capacity after more than 750 cycles.

We have developed a new safety concept which deliberately allows lithium-whiskers to locally short circuit the positive and negative electrodes. The cell needs no separator to prevent this behaviour; the separator is replaced by a porous isolator.

We found that if short circuits in local areas are allowed, there is neither thermal runaway nor destruction of the electrodes or the electrolyte. There are no irreversible reactions which lead to reduction in cell capacity. The cells are fully functional and safe without additional safety-systems.

The outstanding properties of the batteries were demonstrated in complete cells. We presented a 30 s high power discharge with a power of 1475 W kg^{-1}.

After five deep discharge cycles at a discharge cut off voltage of 1.5 V no damage to the cell was observed.

The overcharge characteristics are excellent. After 100% overcharging the capacity increased about 50% compared with the last normal cycle.

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