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Lithium accumulator for high-power applications

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Abstract

A rechargeable bipolar lithium high-energy accumulator based on a novel electrochemical system was developed. The accumulator has a theoretical specific energy of 1070 Wh/kg, which is at the top of the range of all known battery systems. This bipolar high-energy accumulator will exceed the energy content of the known lithium ion battery. Compared with the conventional cell design, the bipolar accumulator design results in a low cell resistance, a low weight and small dimensions.

The charge/discharge curves of a bipolar battery and its five single cells were discussed in this paper. It will be shown, that the cell with the lowest capacity determines the battery's behaviour. The chemistry of the inorganic electrolyte $LiAlCl_4 \times 1.7\ SO_2$ allows the overcharging of single cells.

Laboratory samples can withstand a load of more than 200 mA/cm and combine a high specific energy up to 60 Wh/kg with a high specific power up to 2500 W/kg.
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Keywords: Lithium battery; Bipolar battery; High-power application; Overcharge protection

1. Introduction

Some applications require storage of electric power that must not exceed a definite weight. For example for an electric vehicle the critical component of the system is the battery. To reach an acceptable range, energy storage with high gravimetric energy is needed. On the other hand, for this example, also high specific power is needed to accelerate the vehicle. The combination of a high content of energy related to its mass and high-power capability is best realized in hybrid systems. Fuel cells are able to store high capacities of energy compared to their weight but are not designed to deliver peak power. If both are needed, a hybrid system is the best choice, e.g. combining a fuel cell with a high-power system. If a battery is used as the high-power system, its specific power has to be as high as possible.

Today's high-power battery systems, like nickel/cadmium, lead-acid [1] or super capacitor systems, can deliver specific power in the range of several thousands W/kg but the required specific capacity, e.g. for the super capacitors, are in the range of a only few Wh/kg.

Today, for rechargeable systems, the greatest capacity compared to the battery's weight is realised in lithium-ion systems. But these batteries cannot be discharged with continuous rates higher than 10 C. In this case a specific power of 1350 W/kg is realised [2].

For the combination of the high specific energy of a lithium battery system with the required high power it is necessary to reduce the internal impedance. The bipolar battery design (see Fig. 1) minimizes IR loss between adjacent cells in a cell-stack and provides for uniform current and potential distribution over the active surface area of each cell component.

The main disadvantage of the bipolar construction is the fact that it is not possible to control the potentials of the single cells during the charge/discharge. Due to differences in the electrode's capacity, cell impedance and ageing processes, the state of charge of the individual cells drifts apart after cycling. In this case the cell with the lowest capacity determines the battery's behaviour. If the bipolar battery is charged to the sum of the "end of charge" voltages, two effects can be observed. The single cells with the highest capacities won't be charged to their nominal capacity and the weakest cell can be overcharged. For the lithium-ion systems this results in the destruction of the whole battery system.

To overcome these problems, it is necessary to have an overcharge-protecting system as in the nickel–cadmium

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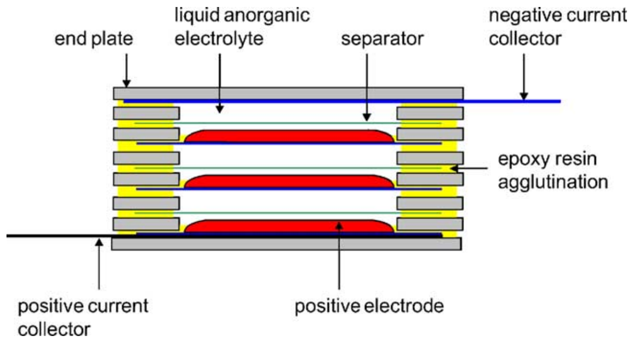

Fig. 1. Bipolar battery design.

batteries, where oxygen is the protecting redox compound.

2. Experimental

The developed rechargeable bipolar lithium high-energy accumulator is based on a novel electrochemical system [3]. The high-power capability of the battery requires the use of an electrolyte solution of high conductivity that is based on a solvate with sulfur dioxide. The transportation of current inside the battery works via lithium ions. There is no metallic lithium in the system in discharged state. The complete usable lithium stock is intercalated in the positive mass (reversibly stored on interstitial sites of the $LiCoO_2$ lattice).

While charging (cutoff voltage is 4.2 V), lithium ions from $LiCoO_2$ are deintercalated, and metallic lithium is plated on the current collector of the negative electrode:

$$LiCo^{III}O_2 \rightarrow Li_{1-x}Co^{(1-x)III}Co^{XIV}O_2 + xLi^+ + xe^-$$

$$Li^+ + e^- \rightarrow Li^0$$

On discharge (average discharging voltage is 3.9 V; cutoff voltage is 3.0 V), the same reactions take place in the reverse direction.

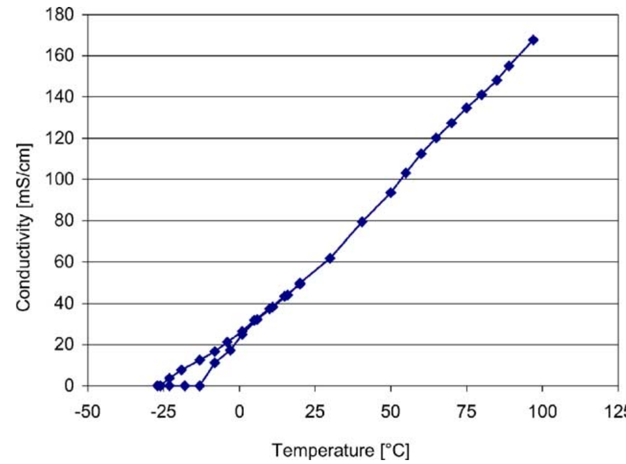

Fig. 2. Specific conductivity of the inorganic electrolyte $LiAlCl_4 \times 1.7\ SO_2$ at various temperatures.

The battery has a theoretical specific energy of 1070 Wh/kg, which is at the top of the range of all known battery systems. This bipolar high-energy accumulator will exceed the energy content of the known lithium ion battery.

The high-power capability of the battery requires the use of an electrolyte solution of high conductivity. The specific ionic conductivity of the 1 M $LiClO_4$ in 1:1 propylene carbonate/dimethyl carbonate and of the inorganic electrolyte $LiAlCl_4 \times 1.7\ SO_2$ at 20 °C are 10 and 50 mS/cm, respectively (Fig. 2).

Another important point designing a bipolar battery is the overcharge protection. The chemistry of the inorganic electrolyte allows the overcharging of single cells. At potentials higher 4.2 V an $AlCl_4^-$ anion will be oxidized at the anode and forms $AlCl_3$ and SO_2Cl_2. Simultaneously, Li is deposited at the cathode. The high solubility of $AlCl_3$ and SO_2Cl_2 in the electrolyte leads to the recombination of the

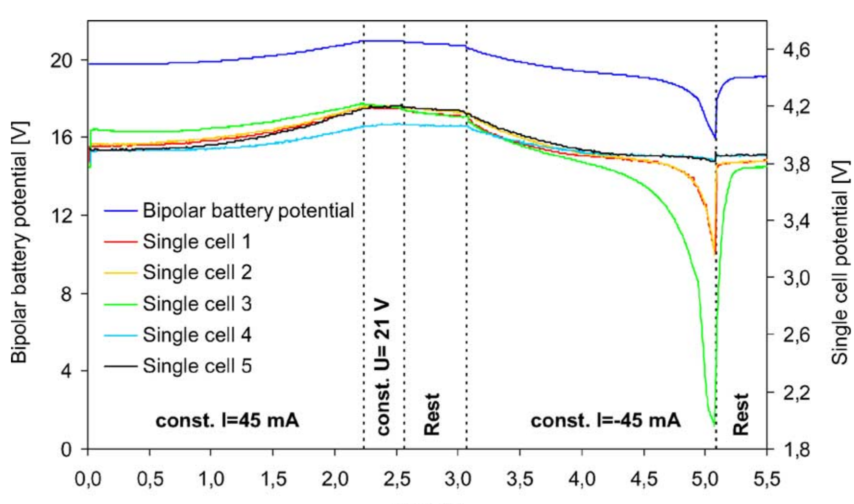

Fig. 3. Charge/discharge curves of a bipolar battery ($Li/LiAlCl_4^* \times SO_2/LiCoO_2$) and its five single cells.

Fig. 4. Laboratory sample of a bipolar battery ($Li/LiAlCl_4^* \times SO_2/LiCoO_2$).

electrolyte salt at the negative electrode:

$$2AlCl_3 + SO_2Cl_2 + 2Li \rightarrow 2LiAlCl_4 + SO_2$$

Bi-functional electrodes are made by application of the electrode material on to a metal foil. These electrodes were stacked together with a separator to form a single cell (Fig. 1). The thickness of the metal foil is the length of the current path and so very short. Compared with the conventional cell design, this results in a low cell resistance, a low weight and small dimensions.

The current collecting happens over the end plates. With this bipolar design it is possible to realize higher potentials up to some hundred volts in one battery stack.

Fig. 3 shows the charge/discharge curves of a bipolar battery (Fig. 4) and its five single cells. The battery has a capacity of 100 mAh. It was charged with a constant current of 45 mA to a cell voltage of 21 V followed by a constant potential charge of 21 V until the current decreases to 8 mA. After a rest time of 0.5 h it was discharged with a current of 45 mA until an end of discharge voltage of 15 V.

The single cells curves show the differences in capacity and electrode performance between the single cells. Single cells 4 and 5 are very similar and have the highest capacity but were not completely discharged. Single cells 1 and 2 are also very similar and show the expected discharge curve. Single cell 3 has the lowest capacity and was discharged to 1.9 V. This cell determines the discharge capacity of the bipolar battery stack. During the charge the cell number 3 has the highest potential and is subjected to overcharge. This overcharge leads to a charge capacity of 120 mAh.

Laboratory samples can withstand a load of more than 200 mA/cm^2. Based on proper design of the battery and charging equipment, the battery can be charged up to 80% of the capacity in 30 min. Due to the high voltage, the energy efficiency is higher than 80%.
Technical data of the laboratory sample:

Number of cells	5
Electrode surface (cm^2)	25
Battery height (mm)	4.5
Battery weight (g)	33
Average discharge voltage (V)	19.5
End-of-charge voltage (V)	21.5
Capacity (mAh)	100
Max. operation temperature (°C)	40
Specific power (W/kg)	2500
Specific energy (Wh/kg)	60

3. Conclusions

A 100 mAh laboratory sample of a bipolar lithium battery with an inorganic electrolyte has been prepared. The development of the single cell potentials during charge/discharge of the bipolar battery clearly shows the different performance of these cells. The weakest cell determines the overall battery capacity and was overcharged without destroying of the cell because of the overcharge protection mechanism of the inorganic electrolyte. Due to the high specific conductivity of the electrolyte and the bipolar design the battery combines a high specific energy up to 60 Wh/kg with a high specific power up to 2500 W/kg.

Acknowledgements

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