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New innovative materials for advanced electrochemical applications in battery and fuel cell systems

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Abstract

The advanced material POLYMET is an innovative high tech polymer with a three-dimensional polymeric structure metallized with an enclosing coating of different kinds of metals or alloys. The result is a range of tailor-made, microporous structures on a designable scale. By varying the metals and alloys, it is possible to draw upon extremely diverse areas of applications such as battery systems, fuel cells, filters or efficient catalysts as well as air regeneration systems, e.g. in aerospace. The three-dimensional structure of metallized high tech woven or non-woven materials or foams causes a lot of advantages such as high conductivity, high corrosion resistance, flexibility or mechanical strength. Therefore, POLYMET is suitable for, e.g. current collectors or gas diffusion layers in energy storage systems. They supply an economic and environmental alternative material to improve functional electrochemical systems.

Keywords: POLYMET; Lithium battery; Fuel cell; Current collector; Gas diffusion layer; Microporous material

1. Introduction

Lithium-ion batteries are most popular in the area of high quality electronic devices because of their high energy density, high voltage and long cycle-life just as fuel cells are for a continuous low emission power supply. POLYMET has been proved as an innovative material with a spread spectrum of functions to improve both energy systems. In lithium-ion batteries, POLYMET was used as a current collector alternative for expanded meshes. The three-dimensional metal structure of the POLYMET achieves an advantageous distribution of collector and active material that becomes noticeable in decreasing internal resistance and significantly increasing current density.

Over the last years, fuel cell systems have become more and more important for a continuous emission free power supply. Fuel cells appeal because of their high efficiency of 50–60% (Carnot-factor: 60–70%) compared with a combustion engine.

The proton-exchanging membrane (PEM) fuel cell takes a key position. This system has the highest efficiency, works without moving parts and is almost maintenance-free. If pure hydrogen is used as fuel only water is developed by cell reactions. But if the fuel contains hydrocarbons (e.g. methane, methanol) CO_2 will be formed however more less then in combustion engines.

In theory, the cell voltage of fuel cells is 1.23 V (voltage of decomposition of water). In practice, the cell voltage is about 0.6–0.9 V because of internal resistance, by-products or poor gas diffusion. Higher cell voltages could be realized by series connection of single cells to so-called stacks.

The core of the PEM fuel cell is the so-called membrane electrodes assemble (MEA). The MEA's are made of a polymeric membrane and a porous carbon material with a catalyst on the surface. Normally platinum or platinum/ruthenium are used as catalyst in scale of 0.1–0.3 $mg\,cm^{-2}$ B. Gas diffusion layers are used for a regular distribution of the gas. These gas diffusion layers have an important influence on the efficiency of the fuel cell system. A poor gas diffusion also a poor current collector lead to an increasing internal resistance and therefore to a decreasing cell voltage [1–4].

POLYMET materials in fuel cells lead to a visible progress. The POLYMET material fulfils the purpose of gas diffusion layer and current collector simultaneously. The internal resistance of the cell is noticeable reduced (Table 1).

2. Experimental

Different investigations are necessary to test the usability of POLYMET materials in lithium batteries or in fuel cells.

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Table 1
Comparison of a lithium-ion battery with standard materials like copper grid as current collector with the same type of battery with POLYMET as current collector

Characteristics	Lithium-ion battery with standard materials	Lithium-ion battery with POLYMET materials
Cell voltage (V)	3.7	4.1
Capacity (mA h)	86.5	130
Battery dimension (g)	4.5 (2.8)[a]	4.5 (2.8)[a]
Energy density (Wh/kg)	70 (115)[b]	115 (185)[b]
Cycle-life (cycles)	>500	>500

[a] The values are in cm^3.
[b] The values are in Wh/l.

2.1. POLYMET in lithium batteries

To analyze the principle suitability of POLYMET in lithium batteries different kinds of POLYMET materials are tested for the swelling behavior in usual battery electrolytes. A swelling or shrinking of the current collector material in commercial electrolytes destroys the electrode and interrupts the regular electrochemical active surface between collector and active material. The volumetric change of the materials can be measured with a dilatometer. The in situ dilatometer records the macroscopic extension (dilation) and contraction of the material in electrolytes. The measurement is based on the change of the resonant frequency of a resonance circuit. The scheme of a dilatometer is shown in Fig. 1.

The spool of the resonance circuit is divided into two parts. The sample is located between two stamps. The lower stamp is fixed and serves as a working electrode, the upper stamp is flexible and transfers modifications of the samples to the upper ferrite shell. If the samples are shrinking or swelling the resonant frequency of the circuit changes. The signal of the changing frequency could be recorded. The calibration of the dilatometer is made with standard metal samples with a definite thickness [5].

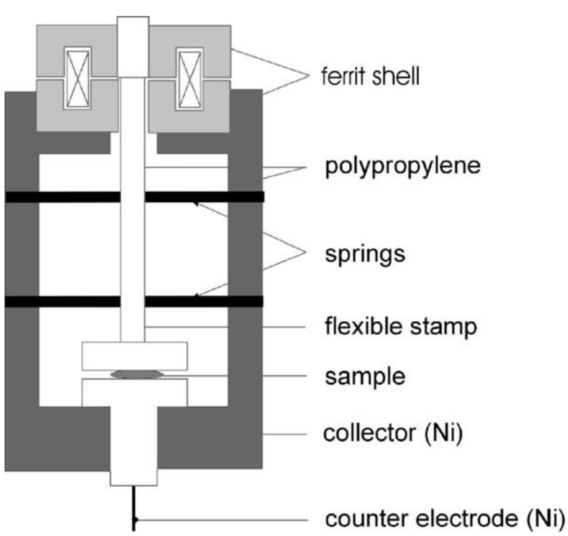

Fig. 1. Scheme of a dilatometer.

In order to compare the electrochemical properties of POLYMET with standard battery materials like copper or aluminum grids the materials have been studied as anode and cathode materials in beaker cells and in complete battery systems.

The behavior of the materials could be characterized with cyclovoltammetric measurements. A constant potential between working electrode (WE) and reference electrode (RE) leads to a Faradaic current between counter electrode (CE) and WE because of the electrochemical reaction. The Faradaic current could be recorded versus the potential in a cyclovoltammogram. Besides qualitative information about reversibility and kinetic of electrochemical processes, it is possible to get quantitative information about the charge of the electrochemical reaction. The charge amount could be calculated from the integral of the current potential curves if the scan $V = dE/dt$ is constant.

For preparation of the active materials commercial battery materials were used, e.g. Graphite KS 6 (Degussa, Germany) or SFG 44 (Timcal, Switzerland) for anodes and lithium spinels $LiMO_2$ (M = Mn, Co, Ni). If not described otherwise $LiCoO_2$ (Merck, Germany) was used in the following investigations. The electrolyte is also a commercial product from Merck, Germany, it is the LP 30 containing EC/DMC 1:1, 1 M $LiPF_6$. Besides the charge/discharge behavior of anode and cathode, materials has been analyzed to confirm the suitability of the POLYMET materials for battery use. Reference measurements have been made on the same mixture of active materials on copper or aluminum grids.

2.2. Preparation of electrodes

The electrodes have been prepared by laminating a slurry of active materials on the one hand onto POLYMET and on the other hand on metal grids.

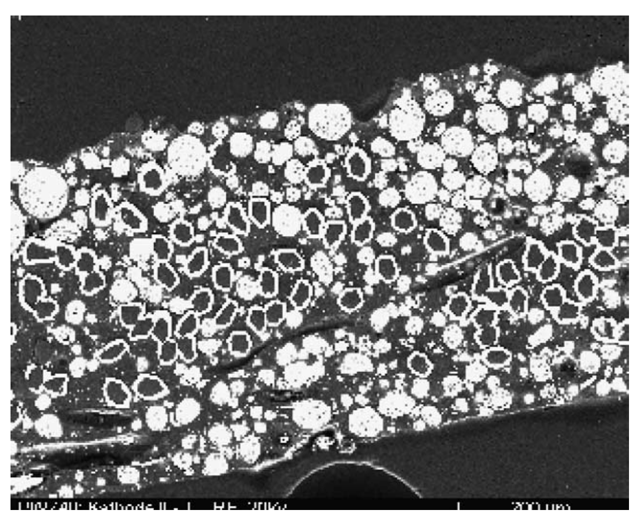

Fig. 2. The SEM picture of a cathode made with POLYMET as a current collector shows the regular distribution of active materials in POLYMET.

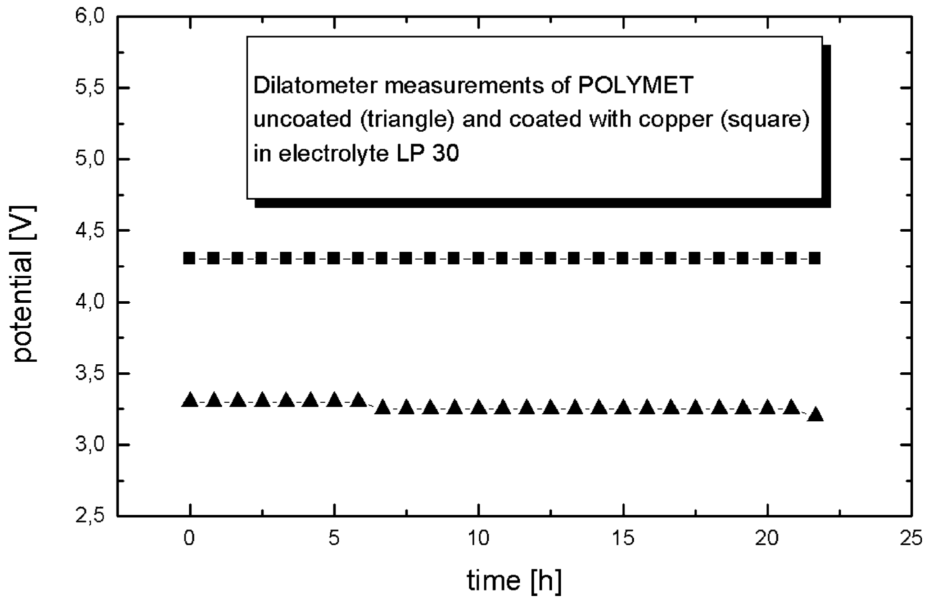

Fig. 3. Dilatometer measurement of POLYMET in a commercial electrolyte like LP 30 (EC/DMC 1:1, 1 M $LiPF_6$).

The active materials for the anodes have been assembled as follows:

- 95 wt.% graphite (Degussa, Germany or Timcal, Switzerland)
- 5 wt.% PVDF (Aldrich)
- *N*-methylpyrrolidone

And the active materials for the cathodes:

- 90 wt.% $LiMO_2$ (M = Mn, Co, Ni)
- 5 wt.% high conductive carbon (Degussa, Germany)
- 5 wt.% PVDF
- *N*-methylpyrrolidone

First the mixture has been stirred over 12 h and afterwards it has been pasted onto the POLYMET and the metal grids. In the following step, the prepared electrodes have been laminated at 140 °C at low pressure. The results are electrodes of about 200–300 μm thickness with a well-balanced distribution of active material into POLYMET resp. onto the grids.

3. Results

3.1. POLYMET in lithium batteries

Fig. 2 shows an electron micrograph of an electrode. It shows the three-dimensional structure of POLYMET which

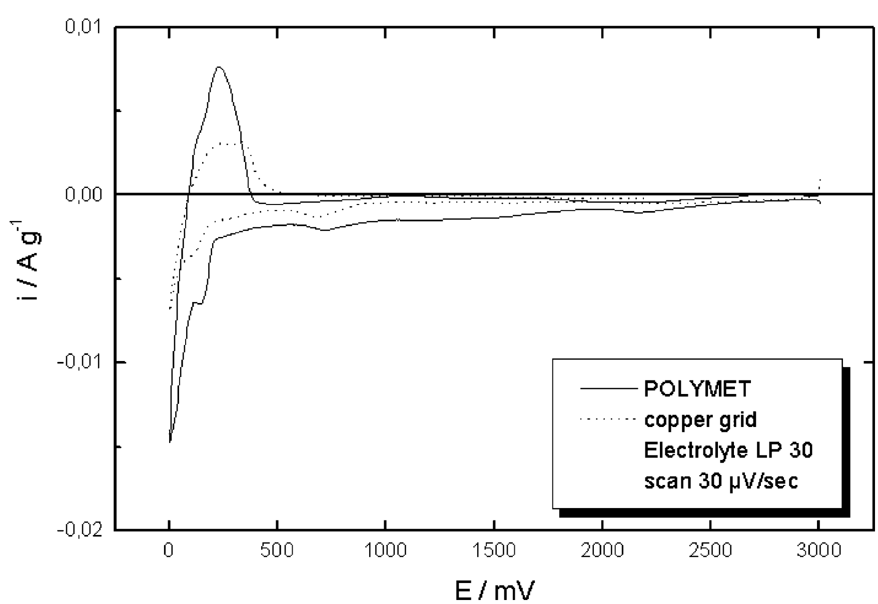

Fig. 4. Cyclovoltammogram of an anode of a lithium-ion battery prepared with POLYMET (solid) as current collector in comparison with s standard lithium-ion battery with same active materials and dimensions but with copper grid as current collector (electrolyte LP 30 (EC/DMC 1:1, 1 M $LiPF_6$)) (dotted), scan 30 μV/s.

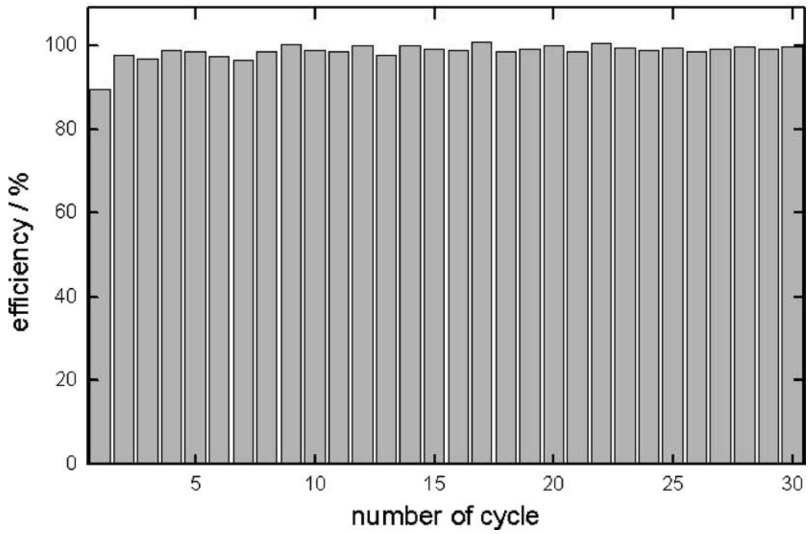

Fig. 5. Charge/discharge curves of a $LiCoO_2$ cathode in LP 30 (EC/DMC 1:1, 1 M $LiPF_6$).

allows to distribute the active material evenly into the current collector material POLYMET. There are no defects or gaps between the active material and collector that could increase the internal resistance and decrease the capacity of the battery systems. But if the active material has been laminated with high pressure into the three-dimensional structure of POLYMET, the advantages of the three-dimensional structure (e.g. the extremely low internal resistance of the electrode) disappears. The slurry must be pasted and laminated carefully.

Because of the results of the measurements with the dilatometer it is noticeable that POLYMET is stable in commercial electrolytes for lithium batteries. The size of POLYMET samples in electrolytes is stable. No swelling or shrinking could be measured, as shown in Fig. 3.

Also the cyclovoltammograms confirm the usability of POLYMET as current collector in lithium batteries. In comparison with the commercial metal grids, it is noticeable that the POLYMET has some important advantages in contrast to metal grids. The current density is increasing clearly and the internal resistance of the electrode is much smaller than the resistance of the electrodes with metal grids (Fig. 4).

These experiments with anodes and cathodes show the advantages of the effect of the three-dimensional structure of

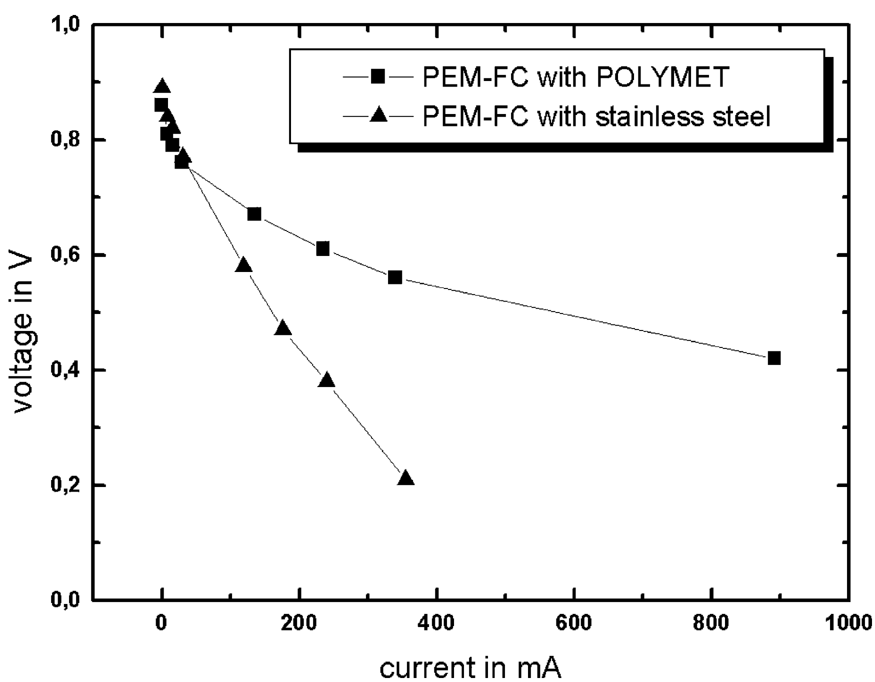

Fig. 6. Current potential curves of a standard PEM fuel cell (triangle) and a PEM fuel cell with POLYMET (square) as a gas diffusion layer and current collector.

POLYMET. The current density of comparable amounts of active masses increases by a factor of 1.5. The POLYMET forms an optimum current collector for battery applications.

The electrodes also shows the characteristic charge/discharge behavior of anodes and cathodes in lithium-ion batteries. In the first cycle, an irreversible loss of capacity is noticeable because of the formation of a thin film at the electrodes in electrolytes like LP 30. This film formation is typical and necessary for lithium batteries to protect the electrode against corrosion and undesirable side reactions and to guarantee the permeability for lithium-ions simultaneously.

The anodes are cycled in a potential range of 0–1.5 V, the charge/discharge current is 20 mA g^{-1}. The cathodes are cycled with same charge/discharge current in the range of 3.7–4.3 V (Fig. 5).

The capacity of the anodes with metal grids, e.g. copper grid is about 210 Ah/kg however the capacity of the same anode with POLYMET is 280 Ah/kg. The theoretical capacity of graphite is about 370 Ah/kg [1,2]. So the POLYMET provides enormous advantages in contrast to metal grids. The remarkable advantages are also noticeable at the cathode side of the battery. Using POLYMET a capacity of 130 Ah/kg is practicable.

3.2. POLYMET in PEM fuel cells

Similar advantages are recognizable using POLYMET in fuel cells. The POLYMET material with the three-dimensional structure was used as current collector and gas diffusion layer simultaneously because of the micro porous structure. The internal resistance of the PEM fuel cell with a Nafion®-membrane, C/Pt catalyst (0.3 mg cm^{-2}) and a surface of the electrodes of 3 cm × 3 cm is noticeable reduced. The current potential curve of a standard PEM fuel cell with a gas diffusion layer and a current collector of stainless steel is shown in Fig. 6 together with the current potential curves of the same PEM fuel cell with POLYMET as current collector and gas diffusion layer.

4. Conclusion

POLYMET represents an excellent alternative material for current collectors in lithium batteries and in fuel cells. An increasing current density, high corrosion resistance, flexibility and a high cycle-life are visible progresses for lithium batteries. In fuel cells, POLYMET leads to a lower voltage drop and therefore to a higher output of the cell unit. In addition, size and weight of the fuel cell system could be minimized by using POLYMET as current collector and gas diffusion layer simultaneously because of the low weight of POLYMET.

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