

Short communication

Fuel cells and batteries: Competition or separate paths?

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Abstract

This article in honor of 60th anniversary of Prof. Dr. J. Garche shows some historical and general aspects of batteries and fuel cells. Our most innovative product PoLiFlex™ will be highlighted and compared with the direct methanol fuel cell (DMFC), which is sometimes considered as a replacement for batteries.

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1. Introduction

The first battery was constructed by the Italian Alessandro Volta in 1800. In 1839 Sir William Grove from England invented the first fuel cell. Although the fuel cell was already discovered in 1839, the concept of the fuel cell was not further developed until the 1950s by military and space travel applications. However, many different battery types were developed and commercialized since 1800. The primary Leclanché element and the lead acid accumulator are still used in daily life. Ref. [1] reviews the developments for commercially available batteries over the last 50 years. Table 1 shows a very brief overview of the history of battery [2–6].

In Scheme 1 the basic principle of a fuel cell is shown. In a “cold burning” hydrogen (H_2) and oxygen (O_2) react to the final product water (H_2O).

In Scheme 2, the principle of a lithium-ion polymer cell is depicted. To avoid the presence of metallic lithium for safety reasons, intercalation graphite for the negative electrode is used. The commonly used cathode material is $LiCoO_2$. While charging the battery, the lithium ions move from the $LiCoO_2$ through the electrolyte (which is a lithium-ion conducting) to the negative electrode. Here they are reduced to Li^0 , which

is intercalated into the two-dimensional layered structure of the graphite. During the discharge step, the lithium is oxidized to Li^+ and moves back to the positive electrode where it is intercalated into the cobalt oxide sub-host structure. This sequence of charge and discharge is the so-called “rocking chair principle”.

Batteries and fuel cells convert chemical energy in electrical energy. The main difference between a fuel cell and a battery is, that in a battery the chemical reactants are already in the cell while in a fuel cell these reactants are supplied from outside.

Table 2 gives an overview of the different types of fuel cells [7].

The direct methanol fuel cell (DMFC) is the most promising fuel cell candidate which could replace a battery. Recently, NEC has announced a laptop with a direct methanol fuel cell. Other companies like Hitachi followed with first demonstrators or prototypes for different applications (e.g. cellular phones or PDAs). But when these devices with methanol fuel cells will be available from series production is not clear yet.

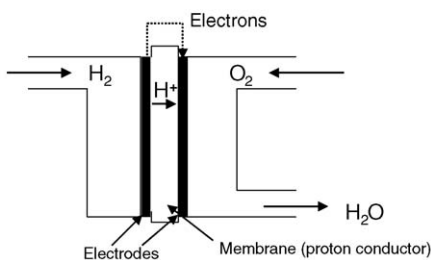
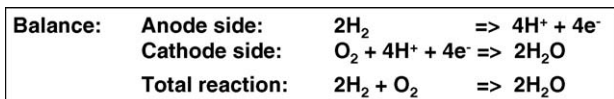
2. Experimental

VARTA PoLiFlex™ batteries were manufactured according to Scheme 3. Every production step can be carried out under ambient conditions, except for the electrolyte dosing,

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Table 1
History of battery

Time	Inventor	System	Remark
1800	Volta	Volta column	First battery. Unit ‘Volt’ named after A. Volta
1839	Grove	Fuel cell (H ₂ /O ₂)	First fuel cell
1868	Leclanché	Manganic	Primary
1902	Jungner	Nickel–cadmium	Rechargeable
1912		Alkalimanganic	Primary
1960s		Lithium	Primary
1980s	Goodenough (AEA technology)	LiMeO ₂ (rocking chair principle)	Lithiated metal oxide
1989	SONY	Lithium ion	First lithium ion battery
1991		Nickel–metal hydride	Series production
1991		Lithium ion	Series production
1994	Bellcore	Polymer lithium ion	Main patent. latest battery technology.



Scheme 1. Principle of hydrogen fuel cell (with membrane).

which is performed under inert gas. The process starts with mixing the raw materials like carbon black, polymer binder, plasticizer and the active materials for the positive and negative electrode in a casting solvent like acetone. This slurry is coated onto a polyester film which is the carrier film. After

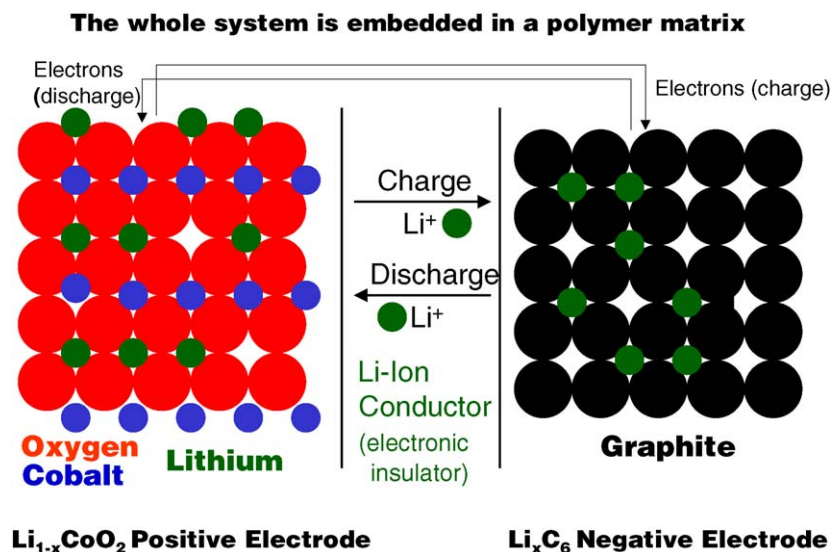
evaporating the casting solvent the electrode sticks to the polyester film and is ready for the following lamination steps. Before the dried cells are activated with electrolyte (usually organic carbonates as solvents and LiPF₆ as conducting salt) the plasticizer has to be removed by an extraction step with an organic solvent.

3. Results and discussion

3.1. Fundamental aspects of the polymer technology

First investigations on a PVdF–HFP-based plastic rechargeable battery were done by Bellcore. In [8] the first practical laboratory polymer cells are described. The base binder polymer for this kind of an advanced plastic technology is the polyvinylidene difluoride–hexafluoropropylene copolymer (PVdF–HFP) which is shown in Fig. 1.

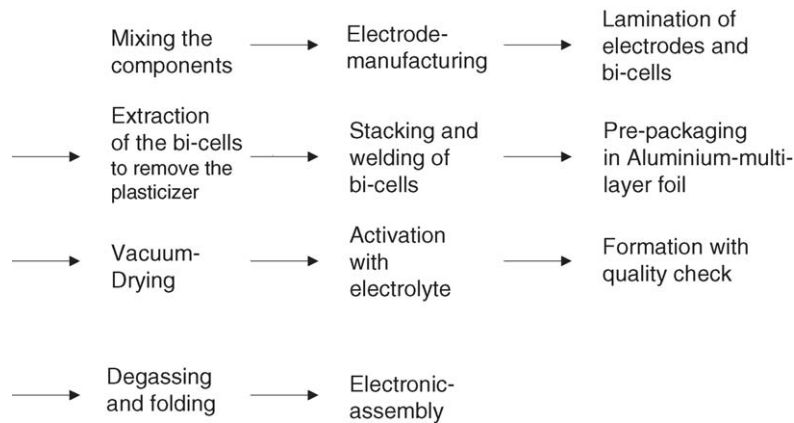
This fluorinated PVdF–HFP binder has a high electrochemical stability and provides a porous electrode structure



Scheme 2. Principle of lithium-ion battery (so-called rocking chair principle).

Table 2
Different types of fuel cells

	T_{work} (°C)	Fuel	Application
AFC alkaline fuel cell	80	Pure H ₂ /O ₂	Space travel, military
PEFC proton exchange fuel cell	80	H ₂ /O ₂ (air)	Space travel, military
DMFC direct methanol fuel cell	80–130	MeOH/O ₂ (air) (liquid)	Potential battery replacement
PAFC phosphoric acid fuel cell	200	H ₂ /O ₂ (air)	Generator
MCFC molten carbonate fuel cell	650	Natural gas, biogas, H ₂ /O ₂ (air)	Generator, stationary power station
SOFC solid oxide fuel cell	800–1000	Natural gas; biogas, H ₂ /O ₂ (air)	Generator, stationary power station



Scheme 3. PoLiFlex™ manufacturing: sequence of process.

together with a plasticizer [9]. Battery grades of this PVdF–HFP copolymer (e.g. Kynar Powerflex® (ELF) or Solef® 21216 (SOLVAY)) have excellent process properties in respect of electrode manufacturing and lamination technique. These PVdF–HFP copolymers can differ in HFP content and molecular weight. The PVdF–HFP in the electrode binds components like carbon black, active materials (LiCoO₂, intercalation graphite) and the plasticizer dibutyl phthalate (DBP). Furthermore the PVdF–HFP provides a good adhesion to the metallic collector. The binder is the key to realize mechanical stable electrodes with a high loading of active materials with relatively low contents of binder itself, carbon black and plasticizer. An optimised binder provides high energy densities for the cell system.

Table 3 shows the dimensions of the different components of the PoLiFlex™ cell. The PVdF–HFP binder is the polymer matrix for different materials, which are in the nano- and micro-scale. To realize high energy density for the PoLiFlex™ the separator, current collectors and the multi-layer packaging foil have to be as thin as possible as long

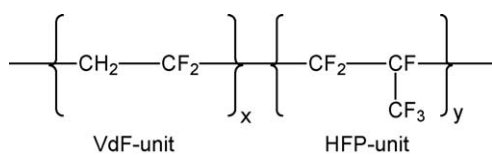


Fig. 1. PVdF–HFP copolymer.

they show no functional disorder in the process or in the final battery.

3.2. Main innovations of the polymer technology

In this paper we want to highlight our further developments of the previous described polymer technology. Before comparing VARTA Microbattery newest polymer-type battery PoLiFlex™ with direct methanol fuel cells we want to introduce VARTA Microbattery PoLiFlex™ and its product properties.

The hot lamination of the collectors to the electrodes and of the separator to electrodes as well leads to a long working time and life time. Especially the 80 °C storage of a fully charged polymer battery (at 4.2 V) gives a good indication on expected shelf life time. Table 4 shows the results of the storage test at 80 °C (PoLiFlex™ fully charged to 4.2 V). The increase of the impedance (at 1 kHz) is rather small even after 96 h storage.

Highest flexible manufacturing of different footprints by programmable cutting tools enables footprints from 34 mm × 41 mm to 50 mm × 90 mm for our VARTA PoLiFlex™ products. A wide range of thicknesses for the batteries (from 0.7 to 5.0 mm) is possible due to the stacking technology. In Table 5 different examples are described.

Based on the polymer technology as described in 3.1 and its further modification and development, VARTA Microbattery GmbH is able to provide PoLiFlex™ in flexible design according to customer's requirements by the so-called form-

Table 3
Excursus on dimensions in a VARTA PoLiFlex™

Material	Dimension (μm)	Remark
Carbon black (single nano-particle)	0.04	Mean particle size
LiCoO ₂	6–10	Mean particle size
Intercalation graphite	15–25	Mean particle size
Cu collector foil (solid foil)	11–13	Thickness
Al collector foil (expanded metal)	37–42	Thickness
Separator	16–25	Thickness
Laminated cathode	90–110	Thickness with Al collector
Laminated anode	140–160	Thickness with Cu collector
Laminated bi-cell	400–500	Smallest cell unit in the polymer stack
Aluminium multilayer packaging foil	110–130	Thickness of packaging foil for the soft-pack

Table 4
Results of impedance behavior of a fully charged (4.2 V) PoLiFlex™ battery

PoLiFlex™ PLF 083562 0.8 mm thickness; Footprint 35 mm × 62 mm (C/2 capacity at 0.5 C 100 mAh)	Impedance at 1 kHz (mΩ)
0 h	272
24 h	323
48 h	352
72 h	372
96 h	375

factor. Further advantages like excellent safety behavior, high rate performance and almost no swelling at elevated temperatures, were already presented earlier [10].

3.3. PoLiFlex™ versus direct methanol fuel cell

From point of a battery producer we want to emphasize two facts raising from the history of batteries before comparing lithium-ion polymer batteries with direct methanol fuel cells.

- (a) Product cycles for new battery systems are decreasing. But once established as mass product, they are produced and implemented for many years.

Table 5
Examples for different VARTA PoLiFlex™ batteries

PoLiFlex™ type	Capacity at 0.5 C in mAh	Dimensions
PLF 263441	290	2.6 mm thickness Footprint 34 mm × 41 mm
PLF 443441	560	4.4 mm thickness Footprint 34 mm × 41 mm
PLF 383562	810	3.8 mm thickness Footprint 35 mm × 62 mm
PLF 423566	990	4.2 mm thickness Footprint 35 mm × 66 mm
PLF 503759	1100	5.0 mm thickness Footprint 37 mm × 59 mm
PLF 395070	1460	3.9 mm thickness Footprint 50 mm × 70 mm

- (b) The time from the basic patent and functional prototypes to a series production is almost a decade in case of lithium ion and lithium-ion polymer. Particularly product development and the up-scale of the production take another several years.

Disadvantages of direct methanol fuel cell are that it is necessary to use very expensive catalysts and membranes and a complicated and expensive controlling process of operation. Beyond that there are still unsolved technical problems arising from the toxicity and safety issue of methanol. The DMFC provides below 1 V output from the system.

One big advantage of lithium-polymer cells (like PoLiFlex™) is that they are meanwhile established and available from series production. Polymer cells are worldwide well tested, accepted and integrated in devices due to a high level of safety. With a very flexible and fast designing they can be integrated into many applications. The prices for batteries and raw materials are decreasing worldwide at the moment. A polymer cell with LiCoO₂ has particular high voltage (4.2 V) in contrast to the DMFC.

4. Conclusion

At the moment PoLiFlex™ batteries show more advantages in comparison to the DMFC.

We estimate that the DMFC for battery-type applications will be earliest ready for series production and worldwide acceptance in 7–12 years. Then, the DMFC will be only found in niche markets, e.g. in operation at places, where the supply with electric current is a problem.

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