



ELSEVIER

Journal of Power Sources 97–98 (2001) 758–761

JOURNAL OF
**POWER
SOURCES**

www.elsevier.com/locate/jpowsour

Microstructure effects in plasticized electrodes based on PVDF–HFP for plastic Li-ion batteries

Aurelien Du Pasquier*, Tao Zheng, Glenn G. Amatucci, Antoni S. Gozdz

Telcordia Technologies, 331 Newman Springs Road, Red Bank, NJ 07701, USA

Received 15 July 2000; received in revised form 8 November 2000; accepted 28 December 2000

Abstract

Positive electrodes for plastic Li-ion batteries were prepared with several PVDF–HFP based binders, using various types and amounts of plasticizers, under a variety of processing conditions. By varying temperature and pressure of the electrode densification step, electrodes exhibiting a wide range of thickness and porosity were prepared. In addition, the effect of plasticizer removal by solvent extraction or evaporation was investigated. The effect of these parameters on the discharge rate capability and the energy density of these electrodes was quantified, and the results were implemented in the simplified plastic battery manufacturing process that resulted in improved battery performance. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Plastic Li-ion battery; PVDF–HFP; Plasticizer; Microporosity

1. Introduction

Plasticized composite electrodes for plastic lithium-ion batteries [1,2] possess several readily adjustable characteristics, e.g. microporosity, the plasticizer type and methods of its removal, that make them a convenient system to study structure–property relationships. For a given thickness and volume fraction of the binder, the active material and the conductive additive, and depending on its microstructure, the rate capability and energy density of an electrode may vary in a wide range.

In the present study, we investigate the effect of several parameters on the microstructure of the electrode. These include the crystallinity of several poly(vinylidene fluoride) (PVDF) based binders with variable hexafluoropropylene (HFP) content, and the effect of the plasticizer (propylene carbonate (PC), di-*n*-butyl phthalate (DBP) or no plasticizer) and its removal method (solvent extraction or evaporation). Changes in the crystallinity of the polymeric binder affected by processing conditions were investigated by DSC, X-ray diffraction (XRD) and mechanical tests.

The effect of microstructure on the physical properties of the electrode was studied by mechanical testing, pore size distribution by mercury porosimetry, specific surface area

and SEM imaging. Further, rate capability (specific power), specific energy and electrochemical stability (capacity fade) of the electrodes was determined as a function of the electrode thickness. Our results indicate that carefully designed plasticized-polymer Li-ion systems can achieve very high specific power and energy values even at low temperatures (-20°C). Their characteristics are fully competitive with those of liquid-electrolyte Li-ion cells based on non-plasticized electrodes.

2. Experimental

Plasticized LiCoO₂-based electrodes were prepared and tested in SwagelokTM cells according to the general procedure described in [3]. The weight ratio of LiCoO₂:binder:conductive carbon in the electrode formulation was kept throughout this study; only the kind and volume of casting solvent and the plasticizer, and the binder type were changed as described in the text. Whatman glass fiber mat was used as a separator, and thin plastic anodes based on a graphitic carbon were used as counter-electrodes. We have previously ascertained that these two components were not rate-limiting. Al and Cu plungers were used as positive and negative current collectors, respectively. A 1 M LiPF₆ EC:DMC (1:1) battery-grade electrolyte (Merck) was used as the electrolyte. Electrochemical measurements on the positive electrodes were performed using a Maccor battery cycler. Cathodes

* Corresponding author. Tel.: +1-732-758-4579; fax: +1-732-758-4372.
E-mail address: adupasqu@telcordia.com (A. Du Pasquier).

were charged for 2 h at a constant current up to 4.20 V, then for 1 h at 4.20 V at a constant voltage, followed by a discharge at various rates to 2.8 V.

3. Results and discussion

3.1. Nature of the binder

Several PVDF–HFP copolymers are available on the market and may be used as binders for plastic lithium-ion battery electrodes. Solubility of these copolymers in acetone and their swelling in lithium battery electrolytes increases with an increasing content of HFP, while melting temperature decreases. A series of positive electrodes were cast using PVDF–HFP binders containing 0, 5, 12 and 15 wt.% HFP. With an initial capacity of ca. 5 mAh/cm², their discharge rate capability was tested up to a 3C rate at room temperature. No noticeable variation or trend was observed for these electrodes. However, when the test cells based on these four PVDF–HFP copolymers were stored at 80°C for 1 h with an excess of electrolyte, their capacity loss increased with an increase in the HFP content in the copolymer binder. It thus appears that plastic electrodes based on PVDF binders with a high HFP content exhibit inferior electrochemical stability at elevated temperatures.

3.2. Effect of the plasticizer

Plasticizers have been used in the electrode formulations to facilitate processing and improve bonding properties. [4] DBP and PC are two examples of plasticizers that may be used with PVDF–HFP copolymers. Their volatility and plasticizing effect is significantly different, with PC being much more volatile (bp 242 versus 380°C for DBP) and markedly more compatible with PVDF. Their plasticizing effect was investigated at the same volume fraction, in electrodes densified under the same conditions and with the plasticizer extracted using diethyl ether. No difference in the discharge capacity and rate capability was observed for these electrodes, and their thickness and porosity were similar (ca. 150 μm and 51 vol.% air, respectively). For comparison, an electrode of the same composition without a plasticizer was cast from a *N*-methylpyrrolidinone (NMP) solution on an Al foil. While having the same discharge capacity per unit area, this electrode was thinner and less porous (~25 vol.% air). The discharge rate capability was found to be slightly lower than that of a PC-plasticized electrode with a similar capacity; we attribute the difference to a lower porosity of the former.

To study the plasticizer volume fraction effect, a series of cathode compositions were prepared with PC weight fractions ranging from 9 to 13%. The discharge rate capability of these electrodes was found to be little affected by the amount of the plasticizer. This result is supported by the observation

that the porosity of the composite electrodes cast in the presence of a small amount of the polymeric binder is not controlled by the amount of plasticizer, but the free packing density of the solids and is always higher than the volume of plasticizer. Typically, the air porosity of such electrodes before the densification step is between 45 and 55 vol.% as observed in SEM images, in which large voids are clearly visible.

3.3. Effect of plasticizer removal method

When PC or other relatively volatile solvent is used as an electrode binder plasticizer, it can be removed either by liquid extraction using a lower boiling solvent such as diethyl ether, methanol, ethanol hexane, etc. or by evaporation at temperatures ranging from 40 to 120°C. The latter process is attractive from a practical point of view, since it allows one to avoid solvent extraction and the need to handle and process large volumes of often flammable solvents, with concomitant cost and safety advantages. Electrodes having various specific capacities (ca. 1.5, 3.5 and 5 mAh/cm²) were cast with three binders (12, 5 and 0% HFP). After densification, they were either dried for 1 h at 70°C in air or extracted in diethyl ether followed by drying.

The following observations were made: the rate capability was more affected by the electrode thickness (electrode capacity) than the kind of binder used or the plasticizer removal method. However, the dried electrodes consistently displayed slightly lower capacity and slightly lower discharge rate capability. To confirm this, the effect of the drying temperature was studied; it was found that the rate and discharge capacity decreased with an increase in the drying temperature. In order to study the observed effects at the polymer level, self-supporting films were cast from a homogenized slurry containing fumed silica, PVDF–HFP (5 wt.%) and PC, in the 3:2.5:3 weight ratio, using acetone as a casting solvent.

Mechanical strength tests performed on these films after solvent extraction or drying at 70°C indicated that the extracted films are significantly more elastic and less brittle than the dried ones. DSC and XRD measurements performed on these films indicated no significant change in polymer crystallinity. Finally, mercury porosimetry and specific surface area measurements using the BET technique performed on various electrode films revealed that the volume fraction of larger-diameter pores decreased significantly in dried electrode films, and that their BET surface area decreased from 2.5 to 1.6 m²/g (Fig. 1). Therefore, we conclude that the change in mechanical properties and the loss in discharge rate capability is caused by a decrease in porosity of the electrodes, which in turn is due to a collapse of the microporous binder structure during heating in presence of the strong PC plasticizer. In order to minimize the loss in discharge rate capability, both the drying temperature and the HFP content in the binder should be minimized. Interestingly, positive electrodes prepared using pure PVDF

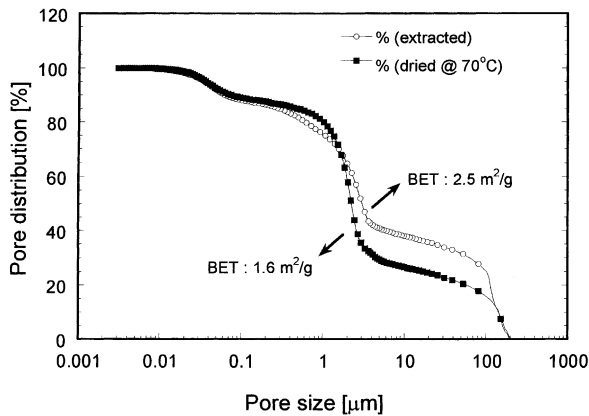


Fig. 1. Pore size distribution of a cathode from which PC was either dried or extracted with ether.

as a binder showed almost no difference in discharge rate capability after drying or solvent extraction.

3.4. Effect of electrode densification conditions

Plasticized electrodes are typically densified under lower pressure than non-plasticized electrodes. This results in electrodes of higher porosity; depending on the densification pressure, the volume fraction of air in the electrodes may vary from 25 to 55%. Since at a constant active material loading per unit area of the electrode, the effects of electrode thickness and electrode porosity counteract each other, we studied the relationship between the electrode energy and power density and its porosity. On one hand, according to Fick's law, reduction of the electrode thickness should decrease diffusion length, and therefore improve discharge rate capability. But, simultaneously, porosity is decreased, which decreases electrolyte content and ionic conductivity in the electrode. To find the optimum densification range, the same electrode having a capacity of 3.5 mAh/cm^2 was densified under a variety of processing conditions, such that its thickness ranged from 80 (25 vol.% air) to $140 \mu\text{m}$ (55 vol.% air). The discharge rate capability at a 2C rate (7 mA/cm^2) was found to increase from 91 to 96% as the porosity increased, although at the same time, the electrode thickness increased too (Fig. 2). However, when we compare the (volumetric) energy density of the electrode samples at a 2C rate, thinner electrodes store 1300 Wh/l , while the most porous electrode studied by us stores only 850 Wh/l .

3.5. Results implementation in plastic batteries

3.5.1. Extractionless cells

It has been shown that high discharge rate capabilities could be preserved in electrodes, where the plasticizer was evaporated instead of dried. The slightly lower values were attributed to a decrease in electrode porosity during drying. When used to build plastic batteries, the cells show a similar

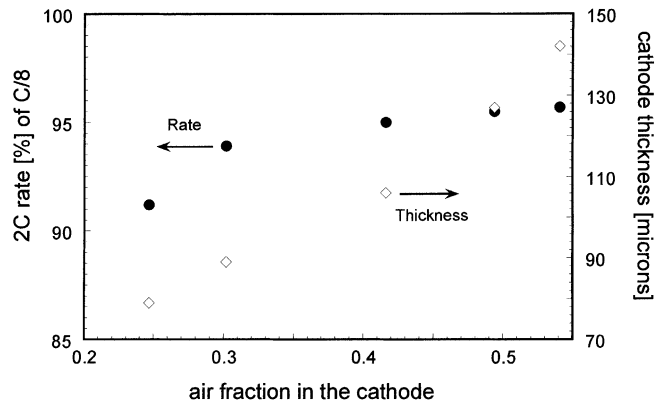


Fig. 2. A 2C utilization and thickness vs. porosity of 3.5 mAh/cm^2 cathodes densified under various pressures.

trend, and the comparison with extracted reference cells shows that the discharge rate capability are very close (Fig. 3), as well as the cycling behavior.

3.5.2. High-rate, high energy density cells

The results of our study carried out on a wide variety of positive electrode compositions indicate that the effective active material loading (mAh/cm^2) has the largest effect on the discharge rate capability of the electrode. To demonstrate this effect, we assembled cells with a nominal capacity of 1.54 mAh/cm^2 , which at a 3C rate (4.6 mAh/cm^2) delivered 88% of their C/8 capacity. Furthermore, our calculations and preliminary experiments indicate that such thin electrodes can be used to build high-discharge rate plastic batteries, such as those used in modern digital cellular phone batteries; small cells ($35 \text{ mm} \times 65 \text{ mm} \times 6 \text{ mm}$, 460 mAh) exhibiting specific energy and energy density of 140 Wh/kg and 310 Wh/l , respectively, have been constructed. When thicker electrodes were used (3.5 mAh/cm^2), prototype cells reached 176 Wh/kg and 446 Wh/l , while capable of delivering 92% of their capacity at a 2C discharge rate.

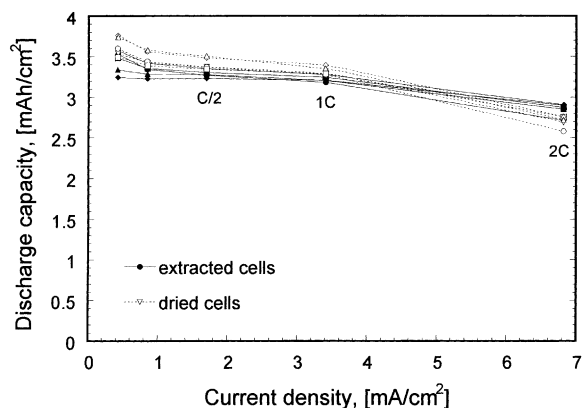


Fig. 3. Discharge capacity vs. discharge current for two groups of PLiON™ cells, processed by extraction or evaporation of the plasticizer.

4. Conclusions

We found that the nature of the PVDF polymer binder, i.e. its HFP content, and the nature, volume fraction and the removal method of an ancillary plasticizer have little impact on the discharge capacity and rate capability of positive electrodes used in plastic Li-ion batteries. This finding is explained in terms of the relatively small volume fraction of pores needed in these electrodes. Thus, a decrease in porosity from 45 to 25% translated into only a 5% decrease in the discharge rate capability at a 2C rate for a series of electrodes characterized by the same, 3.5 mAh/cm², area capacity. Importantly, the small decrease in rate capability was largely compensated by a disproportionally large increase in the volumetric energy density of such densified electrodes. Only very thick electrodes (>5 mAh/cm²) would require more porosity to function effectively. Therefore, the choice of the binder and plasticizer can be driven by other considerations, such as thermal stability, cost, toxicity and ease processing.

In particular, we show that the removal of a lower-boiling plasticizer such as PC by evaporation does not significantly

affect the performance of the positive electrodes. Since the positive electrode was found to be the rate limiting component of the studied batteries, we were able to include such electrodes in high-rate plastic Li-ion batteries processed without liquid solvent extraction. We also found that the electrochemical and mechanical stability of the electrodes during storage in an excess of electrolyte at elevated temperatures can be improved by using a PVDF binder with a lower content of HFP.

References

- [1] A. Du Pasquier, A.S. Gozdz, Proceedings of the Joint 196th Meeting of The Electrochemical Society Incorporation and 1999 Fall Meeting of The Electrochemical Society of Japan, 17–22 October 1999, Honolulu, HI.
- [2] A. Du Pasquier, G.G. Amatucci, I. Plitz, T. Zheng, A.S. Gozdz, J.-M. Tarascon, *Solid State Ionics* 135 (1–4) (2000) 249–257.
- [3] D. Guyomard, J.M. Tarascon, *J. Electrochem. Soc.* 139 (1992) 937.
- [4] US Patent 5,418,091.