

Metallized microporous polypropylene membranes as a support for thin-film electrodes

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Abstract

It is demonstrated that microporous polypropylene separator materials like Celgard® 2400 can be metallized by 'electroless' deposition of thin layers of copper or nickel and subsequent electroplating with any desired metal(s). Electroless metallization on nonconducting materials, is a common process, widely used for decoration of plastics. There is, however, no strong chemical interaction between organic polymers and metals and adhesion is mostly due to mechanical anchoring of the metal layer in cavities of the substrate. In the case of microporous separators as substrate materials, this anchoring effect is extremely strong and the metal layers usually cannot be removed from the substrates without destroying them. As polypropylene is not attacked by common organic, acidic or basic electrolytes, the highly flexible shear- and crease-resistant metal layers on microporous polypropylene support may be used for various battery applications. In particular, 'filling up' the remaining pore structure of single-sided metallized separators with active materials is an attractive route to thin but mechanically-stable electrodes. As an example, electrochemical properties of rechargeable lithium alloy anodes on the basis of copper/nickel-plated Celgard® filled with Sn/Li_xSn are reported.

Introduction

Thin-film electrodes will find applications not only in ultra-thin lithium batteries, e.g., for 'smart cards', but also to meet higher power density requirements, e.g., for electric-vehicle batteries. Double layer capacitors [1] will be a further field of application. Lithium foil suppliers try hard to fabricate commercial quantities of ultra-thin lithium foils [2]. Copper foils from 6–100 μm are manufactured [3] for applications such as 'ion batteries'. Our intention was the development of flexible and mechanically-stable thin-film electrodes consisting of metal layers on a chemically-inert organic polymer support.

Metallizing organic polymer materials by standard methods [4], such as vapour phase or chemical vapour phase deposition usually yields metal layers which cannot resist the attack of electrolyte solutions creeping into the polymer/metal contact area. This is, in particular, true for metal layers in the μm -range which are sufficiently thick

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to be used as current collectors. Composite materials consisting of an inert polymer film and a metal layer linked by adhesives such as polyacrylates are not very suitable for battery applications as the adhesive layers usually are attacked, in particular by organic and basic electrolytes.

Well-adherent metal layers can be produced on microporous support materials by chemical ('electroless') plating procedures [5, 6]. Celgard[®] microporous separator films made by controlled stretching of well-oriented polypropylene films turned out to be a most attractive basis material. Due to the microporous nature of these films, metal layers can be mechanically 'locked' in the tortuous pore structure which is characterized by a distribution of slit-like interconnected channels [7]. If only one side of the microporous separator film is metallized, the remaining porous structure can be filled with electrochemically-active materials. This may be attractive, e.g., for the preparation of thin and flexible lithium alloy electrodes.

Experimental

Celgard[®] polypropylene separator materials [7] were used as a support for electroless-deposited metal layers. Metallization was performed by means of commercial baths (Schering AG, Berlin) [8]. In a first step, Celgard[®] was 'activated' in Neoganth[®] activation solution, an aqueous solution of Pd²⁺ complexes with organic ligand systems. Activation was followed by reduction of adsorbed Pd²⁺ complexes in an aqueous solution containing NaBH₄ and NaOH. This creates small catalytically-active Pd clusters on the Celgard[®] surface. In contact with a solution, containing mainly Cu²⁺ ions and formaldehyde (Noviganth[®] HC), metallic copper is plated on the 'catalyzed' Celgard[®] surface. As Celgard[®] is not properly wetted by aqueous solutions, small amounts of surfactants (e.g., FC 128, 3M-Company) were added if necessary. Higher concentrations of surfactants cause deposition of copper also deeply inside the pores, i.e., the 'penetration depth' of electroless copper deposition can be controlled by surfactants. Apart from copper, various other metals, in particular nickel, can be deposited by similar electroless processes.

Single-sided metallization of Celgard[®] can most conveniently be achieved by using Celgard[®] 2402 as support material. Celgard[®] 2402 consists of two Celgard[®] 2400 separator layers, kept together only by static adhesion forces. After (double-sided) metallization of Celgard[®] 2402, this special separator film can be easily separated in two parts, being metallized on one side only. As 'electroless' plating of copper is a slow process and usually does not yield high-quality copper deposits, a subsequent electroplating step is recommendable. We plated copper and/or nickel (~1–2 μm) as 'reinforcement' on the electroless-copper layer (~250 nm).

Tin was filled into the microporous separator using a conventional tetrafluoroboric acid bath (200 g l⁻¹ Sn(BF₄)₂, 50 g l⁻¹ HBF₄, 25 g l⁻¹ H₃BO₃, 1.5 ml l⁻¹ Triton[®] X-114, 25 °C, 1.5 mA cm⁻²). Antimony, bismuth or zinc fillings can also be obtained by standard plating procedures. Atomic force micrographs were made with a Nanoscope II controller and AFM (Digital Instruments, Santa Barbara, USA). Impedance studies were performed in the controlled current mode, using a Solartron 1174 frequency response analyser. To make up test electrodes for studies of the electrochemical alloying behaviour of metals incorporated in the pore structure of Celgard[®], the samples were fixed on a glass backing. The electrochemical alloying experiments were carried out in 1 M LiClO₄/PC-DME (60–40).

Results and discussion

Figures 1(a) and (b) show atomic force micrographs (AFM) of Celgard® 2400, thickness $\sim 25 \mu\text{m}$, porosity $\sim 40\%$. The surface structure is characterized by slit-like or elliptical pores going through the separator film, with short diameters of about 20–50 nm and long diameters of $\sim 100\text{--}200 \text{ nm}$.

These pores guarantee adhesion of electroless-plated metal layers by providing anchor sites. The copper layer is locked into the microporous polypropylene support (Fig. 2). The dependence of surface resistance on the thickness of the metal layer is shown in Fig. 3. These resistances were measured on test slips, sized 10 by 1 cm in longitudinal direction.

To make up Li alloy electrodes Li_xM , metallized Celgard (single-sided, electroless copper with nickel and/or copper reinforcement) was 'filled' with 'matrix' metals M, like antimony, bismuth, tin and zinc by electroplating from standard aqueous baths. For comparison, the same amounts of these metals were plated onto plain copper foils. These two types of electrodes were submitted to various cycling experiments in organic lithium electrolytes.

It should be mentioned that electrodeposition into the pores of Celgard® is surprisingly uniform as long as it is performed in sufficiently stirred solutions and at relatively low current densities ($0.5\text{--}4 \text{ mA cm}^{-2}$). Stirring limits and levels the thickness of the diffusion layer to the length of the pores. Conditions for metal deposition are obviously very similar in each particular pore. This is certainly related to their uniform

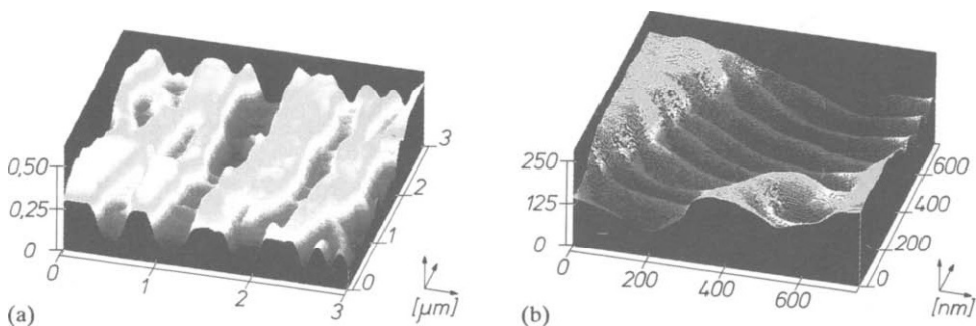


Fig. 1. Atomic force micrograph of Celgard® 2400 separator surface: (a) low resolution, and (b) high resolution.

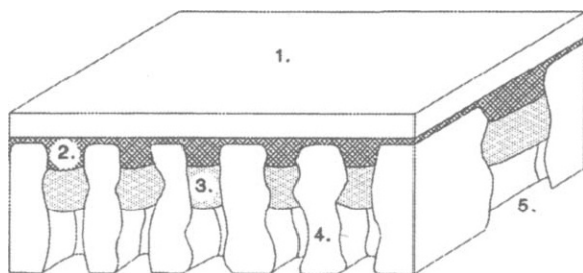


Fig. 2. Schematic diagram of the composite electrode: (1) reinforcement; (2) electroless copper; (3) matrix metal; (4) Celgard® 2400, and (5) pore.

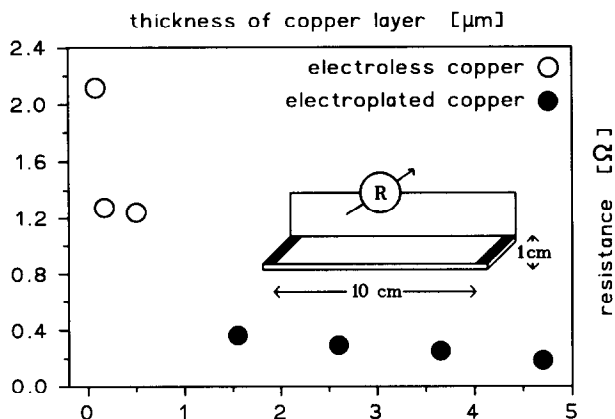


Fig. 3. Surface resistances of copper films on Celgard® 2400.

geometry. Moreover, inside the micropores there is simply 'no choice' between 2d and 3d growth. Surfactants in the plating bath are required because of the hydrophobic character of Celgard®.

In this paper, results of cycling experiments with lithium-alloyed tin-filled Celgard®/copper composites and with tin layers on copper foil will be presented in more detail. Experiments were performed in pyrex cells and electrodes were set up in an 'open' configuration, i.e., they were not packed or protected by separators but simply immersed vertically in an excess of electrolyte. Battery-grade lithium foil was used as counter electrodes. The charge/discharge reaction is represented by eqn.(1) (x_{\max} being 4.4 [9]):



As it is well known, full capacity cycling of thin layers of lithium-alloying metals on an inert support causes bad problems because the contact between inert substrate and alloying material suffers during cycling [10–13]. This is mostly because of crack formation due to the drastic changes in volume related to the insertion and removal of lithium. The cracks enable the electrolyte to penetrate into the inert/active interface and finally to 'film' the Li_xM surface by electrolyte decomposition products separating the active material from the inert support.

These undesired effects can be significantly reduced by composite electrodes based on microporous polypropylene. This is illustrated by Fig. 4(a) showing a constant current cycling experiment with tin-filled Celgard® 2400, having a nickel-reinforced copper backing. For comparison, the results are shown for tin deposited directly on copper foils (Fig. 4(b)).

We believe that the improvement is due to the fact that (i) the microparticles of Li_xM are 'packed' and kept together in a relatively soft polypropylene matrix, and (ii) they will not be cracked during cycling as their absolute changes in dimensions are very small. It should also be noted that the cycling conditions used in this study may be regarded as an accelerated deterioration test. Commercially-available rechargeable lithium batteries with lithium alloy are designed for very flat cycling only.

It might be argued that the rate capabilities of Celgard®/ Li_xM composite electrodes will be low, because of the considerable fraction of passive polypropylene (~60 vol.%).

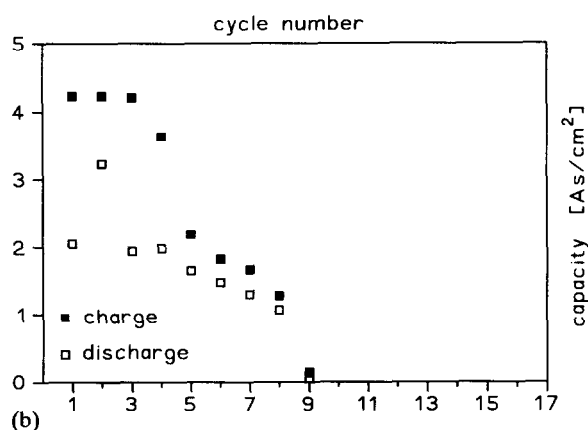
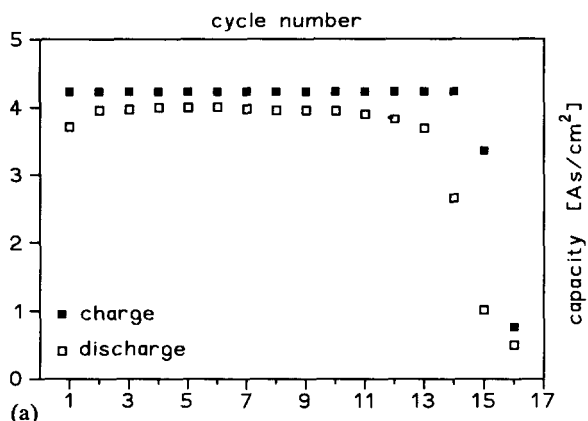


Fig. 4. Constant-current cycling experiment with: (a) tin-filled Celgard® 2400, and (b) tin on a copper foil. $i_c = i_d = 0.1 \text{ mA cm}^{-2}$, cutoff: $+0.01/+1.6 \text{ V vs. Li/Li}^+$; utilization of total tin supply $\sim 50\%$.

Impedance studies of Celgard®/Li_xSn and copper/Li_xSn electrodes, respectively, clearly indicate that with respect to charge-transfer resistance the negative effect of passive polypropylene is even overcompensated (Fig. 5). On the other hand, diffusion resistances of composite electrodes Celgard®/Li_xM and plain electrodes copper/Li_xSn seem to be comparable. This is also corroborated by galvanodynamic polarisation studies ('current ramp' studies) at high load. We assume that this is caused by an increase in real surface area. Apparently not only the top but also a part of the mantle of the Li_xSn 'pillars' inside the polypropylene membrane is accessible to the electrolyte solution.

Conclusions

Highly flexible and shear- and crease-resistant thin-film electrodes can be fabricated on the basis of electroless-metallized microporous polypropylene separators. The microporous structure of single-sided metallized separators can be used to accommodate and support lithium-alloying metal matrices. Alloy electrodes of this kind show improved

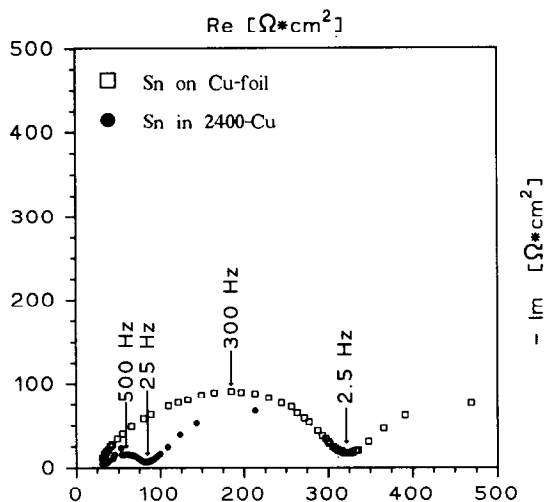


Fig. 5. Impedance plot of tin-filled Celgard® 2400 and tin on copper foil during charge, $i_c = 0.1 \text{ mA cm}^{-2}$, utilization of tin $\sim 25\%$.

cycling behaviour compared with thin-film alloy electrodes supported by plain metal foils only.

Acknowledgement

Support of this work by Silberkraft Leichtakkumulatoren GmbH, Duisburg, Schering AG, Berlin, Deutsche Forschungsgemeinschaft, Bonn and Fonds der Chemischen Industrie is gratefully acknowledged.

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