Substrate-induced coagulation (SIC) of nano-disperse carbon black in non-aqueous media: a method of manufacturing highly conductive cathode materials for Li-ion batteries by self-assembly

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Received 02 September 2004; accepted in revised form 25 October 2004

Key words: carbon coating, composite electrode, dip-coating, Li-ion battery, non-aqueous dispersion, substrate-induced coagulation (SIC)

Abstract

Substrate-induced coagulation (SIC) is a coating process based on self-assembly for coating different surfaces with fine particulate materials. The particles are dispersed in a suitable solvent and the stability of the dispersion is adjusted by additives. When a surface, pre-treated with a flocculant e.g. a polyelectrolyte, is dipped into the dispersion, it induces coagulation resulting in the deposition of the particles on the surface. A non-aqueous SIC process for carbon coating is presented, which can be performed in polar, aprotic solvents such as N-Methyl-2-pyrrolidinone (NMP). Polyvinylalcohol (PVA) is used to condition the surface of substrates such as mica, copper-foil, silicon-wafers and lithiumcobalt oxide powder, a cathode material used for Li-ion batteries. The subsequent SIC carbon coating produces uniform layers on the substrates and causes the conductivity of lithiumcobalt oxide to increase drastically, while retaining a high percentage of active battery material.

1. Introduction

Substrate-induced coagulation (SIC) is a relatively new and widely applicable method for coating any kind of surface (e.g. ceramic, polymer, glass, metal) with fine particulate materials [1–4]. It produces a self-assembled and almost binder-free coating of surfaces with small particles. The method is well established for aqueous systems and can thus be used for any kind of materials that are stable in water.

The SIC process (Figure 1) involves the conditioning of a substrate surface with a thin layer of polyelectrolyte. In the second step, the conditioned substrate is dipped into a dispersion of particles (e.g. carbon black or metal oxides), whose stability has been adjusted by addition of a surfactant and an electrolyte. The polyelectrolyte or polymer on the surface destabilizes the dispersion and induces coagulation of the particles.

The process can be repeated as many times as required to produce thicker coatings. The typical thickness of a layer after a single coating is ca. 200 nm [4]. The SIC method has been used to manufacture highly conducting composites, e.g. for battery electrodes, by coating of nonconducting (polypropylene, PTFE) or poorly conductive (manganese dioxide) particles with highly disperse particles of conductive materials, such as carbon black, before production of the composites [5, 6]. Layers deposited by this technique can also be applied for example in electromagnetic wave shielding or as part of the through-holes metallization process in the fabrication of printed wiring boards [3, 7].

Bele et al. refer to a similar coating method they call “Substrate Induced Deposition” or “Novel Coating Technology” (NCT). Their process involves covering a surface (e.g. printed wiring board PWB) with a thin gelatin film. Dipping the substrate into a dispersion, adjusted by surfactant and salt concentration, leads to a deposition of carbon black [8–10].

Because of the low conductivity of LiCoO2 and LiNiO2 which are used as active cathode material in Li-ion batteries, conductive materials such as carbon blacks and graphites are usually added to composite electrodes in order to achieve a higher reversible capacity. Conventional fabrication of carbon black modified electrodes entails the mechanical mixing of carbon black and the active material [11–13]. NCT (see above) was also used to coat cathodes for Li-ion batteries by adsorbing a thin film of gelatin on the active battery material that acts like a glue and induces a deposition of carbon black on the surface [14].

Hong et al. found a better cycle performance for composite electrodes containing LiCoO2, a similar-shape micron-sized graphite and nano-sized carbon black. The uniformly dispersed graphite enlarges the
active surface area of LiCoO₂. Addition of smaller particles of carbon black fills the voids between the active material and the graphite grains, and improves the cathodic performance resulting in a higher discharge capacity [15].

In the optimum case, the carbon black should cover the whole surface of the active-material particles as thinly as possible. Recently, Dominko et al. found the reversible capacity for active cathode materials such as LiMn₂O₄, LiFePO₄ and LiCoO₂ to increase drastically using the NCT with carbon black and maintaining a carbon black concentration of 2%. The uniformity of the carbon black distribution is believed to significantly improve the cathode kinetics [16].

A major disadvantage for the SIC coating process, so far, has been that materials sensitive to hydrolysis could not be coated by the SIC process. The acceptable limit for trace water in non-aqueous batteries is 20 ppm and so the SIC process will only find practical application for coating of active-materials used in Li-ion batteries (such as LiNiO₂ or LiCoO₂), if it can be performed in aprotic, non-aqueous solvents. In order to find controlled hetero-flocculation, non-aqueous dispersions of silica were investigated by Vincent et al. using a particle-bridging mechanism. One set of silica particles contained an acidic co-polymer, whereas the second set of smaller particles contained a co-polymer with basic groups. The interaction of the two polymers caused the silica particles to flocculate [17]. Non-aqueous SIC could also be applied in the fabrication of solar cells or in the field of heterogeneous catalysis. In both cases layers of fine particulate materials are required, which might be moisture sensitive.

Here we report on a SIC method to coat LiCoO₂, the cathode material in Li-ion batteries, in non-aqueous media. The stabilities of carbon black dispersions in NMP have been studied as well, in order to find suitable conditions for the non-aqueous SIC. The results will be reported elsewhere.

2. Experimental

2.1. Chemicals

Commercially available Printex L6 carbon black (Degussa, Frankfurt, Germany) was used to coat mica (Gröpel Elektronenmikroskopie, Austria), copper-foil (Schlenk, Germany), silicon-wafer and LiCoO₂ (Selectipur, cathode powder SC 15, Merck, Germany). Printex L6 is a highly conductive carbon black with a 265 cm² g⁻¹ Brunauer, Emmet and Teller (BET) surface area and an average primary particle size of 18 nm (data supplied by Degussa). Polyvinylalcohol 7200 (PVA, Merck, Germany) and Polyvinylalacetate (PVAc, Fa. Höfferer, Austria) were used as a conditioning polymer and N-Methyl-2-pyrrolidinone (NMP, 99%, Aldrich) as a solvent. LiCl (Merck) was used as electrolyte. Teflon powder (PTFE, Kynar 761, Atofina, USA) was used as a binder and graphite (KS6, Timcal. Corp., Switzerland) as a conductive additive in the composite electrodes.

2.2. Methods

2.2.1. Atomic force microscopy (AFM)

A NanoScope III (Digital Instruments, Santa Barbara, CA, USA) was used for the experiments. Tapping mode was employed to prevent damage of the soft coatings such as PVA and PVAc.

2.2.2. Ellipsometry (ELL)

The instrument was provided by J.A. Woollam Company (VASE model, NE, USA) and was equipped with a monochromatised high-pressure xenon arc lamp as light source and a rotating analyser. An auto-retarder was used to give more exact results for Δ, especially around 0° and 180°. The experiments were done over a range of 300–1100 nm at an incidence angle of 50° and 60° using the auto-retarder. The number of measurements at each wavelength was 20. The Cauchy equation was used to fit the refractive index n to the wavelength λ.

\[ n(\lambda) = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} \]  

2.2.3. Scanning electron microscopy (SEM)

The SE micrographs of copper, mica and silicon-wafers were made with a LEO DSM 982 GEMINI. Field