

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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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

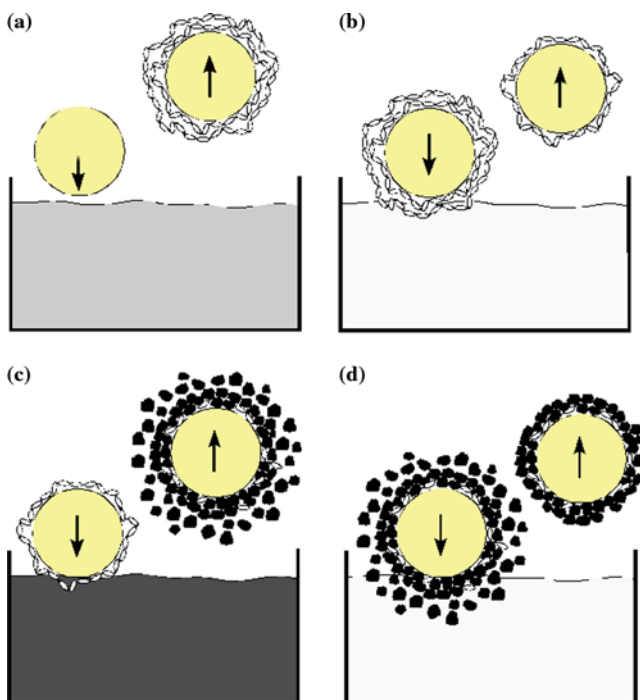


Fig. 1. Substrate-induced coagulation. The substrate is dipped into a polyelectrolyte solution to condition the substrate surface (a); rinsing removes unbound polymer (b); the conditioned surface is then dipped into a dispersion of particles that coagulate on the surface (c) and rinsed again to remove unbound particles (d).

active surface area of LiCoO_2 . 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 LiMn_2O_4 , LiFePO_4 and LiCoO_2 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 LiNiO_2 or LiCoO_2), 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 LiCoO_2 , 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 LiCoO_2 (Selectipur, cathode powder SC 15, Merck, Germany). Printex L6 is a highly conductive carbon black with a $265 \text{ cm}^2 \text{ g}^{-1}$ 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 Polyvinylacetate (PVAc, Fa. Höpferer, 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 . The variables a , b and c are fitting parameters.

$$n(\lambda) = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} \quad (1)$$

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

emission technique (FESEM) was used. The electron beam is thereby generated by very high electric field strengths ($>107 \text{ V cm}^{-1}$) at the surface of the emission cathode. The resulting electron beam is strongly bundled with a diameter of a few Å. This provides very high resolutions and allows the use of low accelerating voltages. LiCoO_2 was characterised with a CAMSCAN CF44 FESEM (field emission SEM, Camscan, Cambridgeshire, UK). The samples were first coated using a carbon arc sputter coater, then imaged at various kinetic energies ranging from 7 kV to 15 kV. The sample was also tilted 30° to the electron beam in the chamber to reduce effects of sample charging.

2.2.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded using a Physical Electronics PHI 5400 spectrometer (Physical Electronics, MN, USA), with a Mg K_α radiation source ($h\nu = 1253.6 \text{ eV}$) operating at 15 kV and 300 W. The X-ray source was not monochromated. Survey spectra were recorded for the region 0–1100 eV at a pass energy of 93.9 eV and resolution of 0.4 eV per step. Multiplex spectra were recorded for selected photoelectron peaks at a pass energy of 29.35 eV and resolution of 0.125 eV per step. During each analysis, the sample stage was cooled with liquid nitrogen to provide a base pressure of 5×10^{-8} torr inside the sample chamber. Because of the insulating properties of some samples, these became charged during analysis, causing the photoelectron peaks to shift to artificially high binding energy. The charge shift was determined from the observed binding energy of the C–H component to the C 1s peak, which has a value of $284.8 \pm 0.2 \text{ eV}$ before charging [18]. All binding energies listed in this report have been corrected for charging. Atomic concentrations were obtained from the experimental peak area using the atomic sensitivity factor of each element [19].

2.2.5. Thermogravimetric analysis (TGA)

TGA measurements were done using an Auto TGA 2950 Universal V 3.38 thermal analyzer (TA Instruments, DE, USA) with an oxygen flow rate of 50 ml min^{-1} and a heating rate of $10^\circ\text{C min}^{-1}$ over the temperature range 20–600 °C.

2.2.6. Specific conductivity by van der Pauw

The van der Pauw method [20] was used to determine the conductivities of composite electrodes containing SIC-coated and uncoated LiCoO_2 . The disc-shaped composite electrode pellets were pressed with 10 t cm^{-2} . The pellets were 15 mm in diameter and 1.2–1.6 mm in height and weighed approximately 1 g.

2.2.7. Carbon black dispersion

For the carbon black dispersion, 1 wt.% of carbon black was added to NMP containing 0.02 mol l^{-1} LiCl. The dispersion was stirred for 5 min, ultra-sonicated for 15 min and stirred with a homogenizer for 5 min.

2.2.8. Non-aqueous substrate-induced coagulation

The surfaces were cleaned with surfactant and ultra-sonicated in water and acetone, dipped into a slowly stirred solution of 0.2 wt.% polyelectrolyte in NMP for 5 min, rinsed twice with NMP and then dried. The pre-treated surface was washed three times with NMP to remove unbound polymer. The sample was dipped into the carbon black solution and stirred for 5 min. The coated surface was washed with NMP and dried under vacuum for 2 days.

3. Results and discussion

The SIC coating process requires a dispersion which is meta-stable. Its stability should be such that it is easy to handle in the laboratory, but also close to the point where coagulation can occur. Carbon black can be dispersed in NMP without any surfactant. The dispersions are stable over several weeks and require the addition of an electrolyte (LiCl) to decrease their stability to a point which makes them suitable for use in the non-aqueous SIC process. The polyelectrolyte or polymer used for the conditioning of the surface has to be soluble in a suitable aprotic solvent and must adhere to the substrate surface.

3.1. Conditioning of the substrate surface

NMP solutions of polyvinylalcohol (PVA) and polyvinylacetate (PVAc) were used to condition copper foil and mica slides. An AFM image of mica conditioned with PVA and subsequently coated with carbon black is shown in Figure 2. The carbon black layer seems to be homogeneous and to cover the whole surface. A scanning electron micrograph of a non-aqueous SIC coated sample of copper foil which had been conditioned with PVA shows a similar uniform carbon black coating (Figure 3). Conditioning of the mica surface with PVAc results in a less homogeneous carbon coating containing agglomerates (Figure 4). Agglomerates of carbon black can also be clearly seen in the scanning electron micrograph of a PVAc-conditioned and non-aqueous SIC-coated sample of copper foil in Figure 5.

Ellipsometry was used to determine the thickness of the PVA and PVAc layers. Because of their flat surface, mica slides were chosen as substrate. The mica slides (diameter 1 cm, thickness 0.5 mm) were dipped into a 0.2% solution of polymer (PVA or PVAc) in NMP for 2 min and then rinsed twice with NMP and dried. Refractive indices were determined for both the coated and the untreated surface. The thicknesses were found to be $49.1 \pm 20.9 \text{ nm}$ for PVAc and 39.86 ± 1.47 for PVA on mica. Compared to PVA, PVAc has a thickness-error 10 times larger than the PVA layer, indicating that the PVA-layer is more uniform than the PVAc layer. These results are in agreement with the morphology found by AFM and SEM. NMP has a dielectric constant lower than water and so polyelectrolytes such

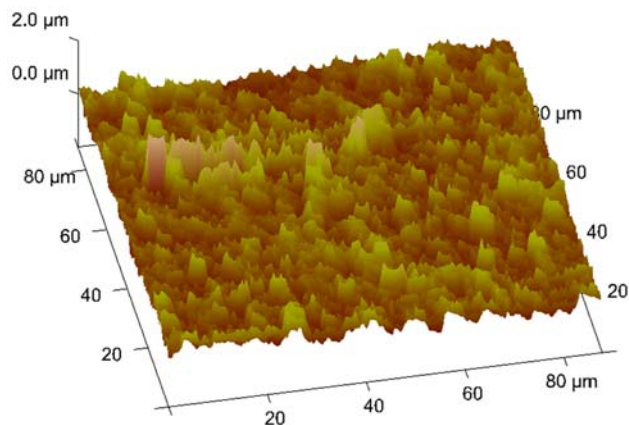


Fig. 2. AFM image of mica conditioned with polyvinylalcohol (PVA) and coated with carbon black by non-aqueous SIC.

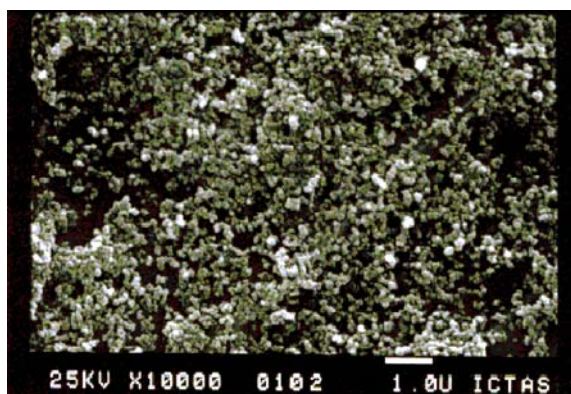


Fig. 3. Scanning electron micrograph of copper foil conditioned with PVA and coated with carbon black by non-aqueous SIC. Scale bar is 1 μm .

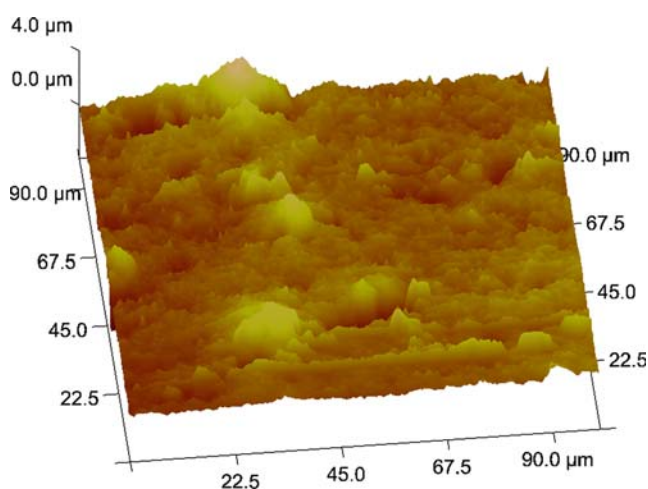


Fig. 4. AFM image of mica conditioned with polyvinylacetate (PVAc) and coated with carbon black by non-aqueous SIC.

as PVAc with high surface charges tend to form agglomerates more easily in organic solvents than in water. This may result in a less uniform coating of PVAc compared to PVA, which bears fewer surface charges. Conditioning of the surfaces with PVA produces more homogeneous coatings in the non-aqueous SIC than

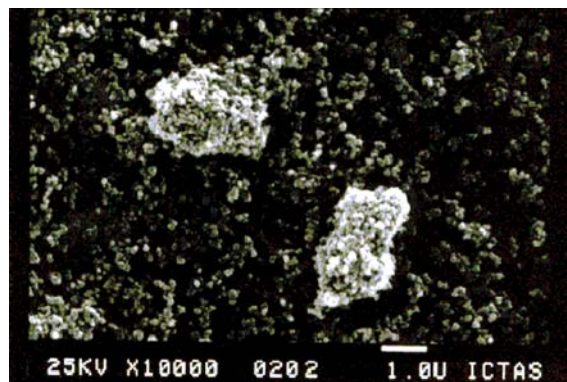


Fig. 5. Scanning electron micrograph of copper foil conditioned with PVAc and coated with carbon black by non-aqueous SIC. Scale bar is 1 μm .

conditioning with PVAc. Therefore, only PVA was used in all further non-aqueous SIC experiments.

3.2. Carbon coating on different surfaces

Mica and silicon-wafers were cleaned and conditioned with PVA as described above. Conditioned and bare mica and silicon surfaces were analysed by XPS together with a sample of neat PVA. The results are summarised in Tables 1 and 2. A comparison of the chemical compositions of the bare and the conditioned mica and silicon surfaces shows that the relative concentrations of elements only present in the substrate have decreased for the conditioned samples. For elements present in the substrates as well as in PVA concentrations are found which are in between those of the bare substrate and PVA. Nitrogen is thought to originate from traces of NMP, whereas carbon on the bare substrates is the result of adventitious contamination. The analyses indicate, that the treatment of these different types of surfaces with NMP solutions

Table 1. Element concentrations from XPS analyses (atom%)

	Mica	PVA	PVA-coated mica
C 1s	30.5	67.2	45.5
O 1s	42.3	32.5	33.5
Si 2p	12.5	–	5.6
Al 2p	9.6	–	5.3
K 2p	2.9	–	2.4
Cl 2p	0.6	–	1.5
Na 2s	0.9	0.2	2.4
N 1s	0.5	–	3.0

Table 2. Element concentrations from XPS analyses (atom%)

	Si-wafer	PVA	PVA-coated Si-wafer
C 1s	19.2	67.2	41.0
O 1s	41.2	32.5	32.2
Si 2p	39.7	–	25.3
N 1s	–	–	1.5

of PVA results in the immobilisation of PVA on both surfaces. Conditioned and bare mica and silicon samples were then dipped into a dispersion of carbon black in NMP and rinsed three times with neat NMP. After drying the samples were analysed by SEM. The SE micrographs of the conditioned mica and silicon surfaces show extensive coverage with carbon black (light areas in Figures 6 and 7). The SE micrographs of the mica and silicon surfaces which had not been conditioned with PVA show only a few spots of carbon black, which accidentally adheres to the surfaces (Figures 8 and 9). Clearly, conditioning of even such different types of surfaces as mica and silicon with PVA leads to extensive coagulation of carbon black particles dispersed in a non-aqueous solvent. A SEM of a carbon black agglomerate on mica with higher magnification shows the nano-disperse nature of the particles (Figure 10).

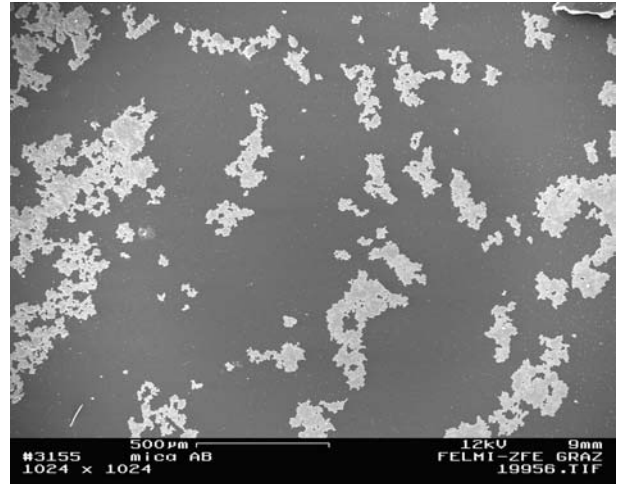


Fig. 8. SEM image of carbon coated un-treated mica. Scale bar is 500 μm .

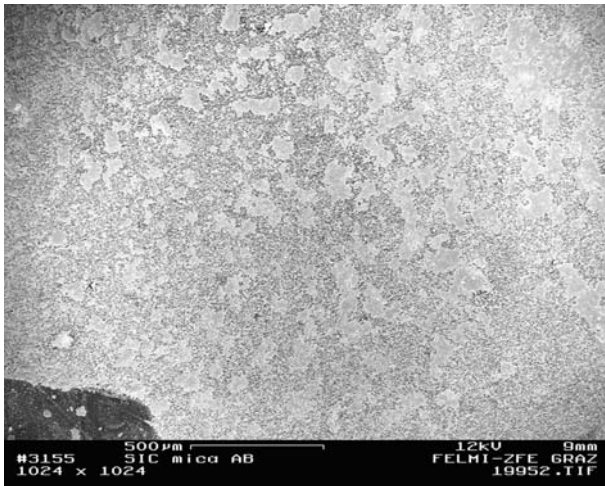


Fig. 6. SEM image of carbon coated PVA-treated mica. Scale bar is 500 μm .

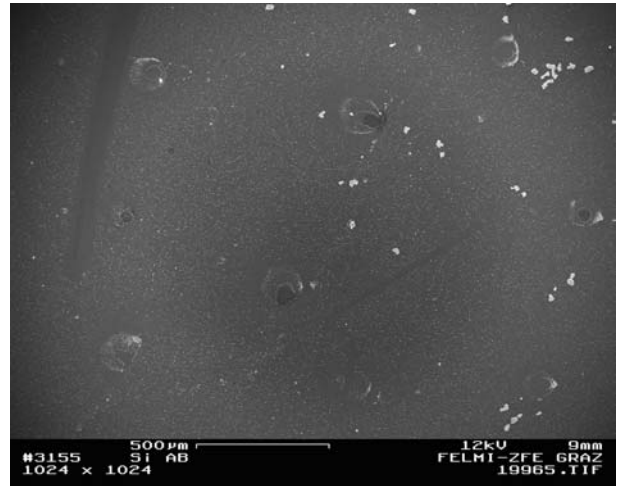


Fig. 9. SEM image of carbon coated un-treated Si-wafer. Scale bar is 500 μm .

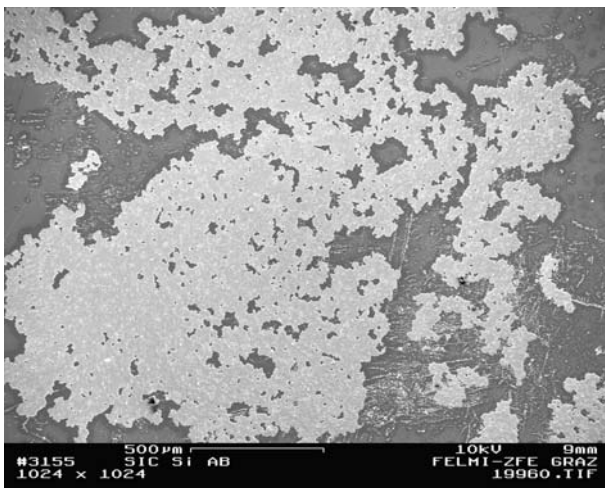


Fig. 7. SEM image of carbon coated PVA-treated Si-wafer. Scale bar is 500 μm .

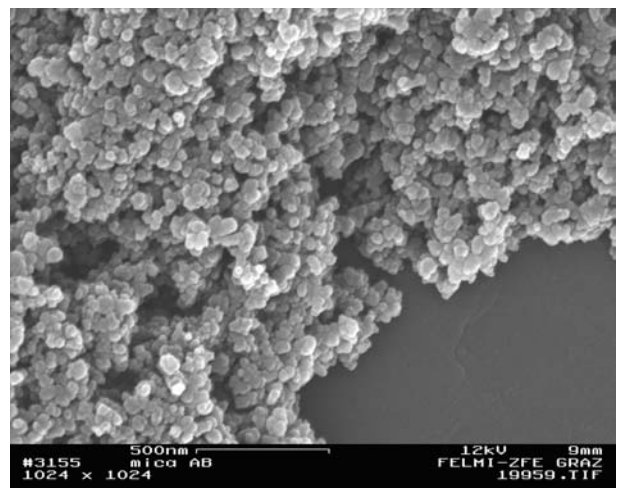


Fig. 10. SEM image of carbon coated un-treated mica. Scale bar is 500 nm.

3.3. Adsorption of PVA on lithium cobalt oxide

A 0.2 wt% PVA/NMP solution was prepared by dissolving 200 mg of PVA (Mowiol 80–98) in 100 ml of NMP at 60 °C. The solution was used at room temperature. LiCoO₂ (12 g) was stirred in the solution for 5 min. The powder was separated from the supernatant using a glass frit and a pump, and rinsed twice with NMP. The coated LiCoO₂ was dried in vacuum for 2 days and then analysed by XPS.

Survey spectra of uncoated LiCoO₂ showed peaks originating from C, Co, O and Li (C originates from adventitious hydrocarbon contamination). The survey spectrum of PVA contained peaks from C, O, as well as Na. Photoelectron peaks for these three elements, as well as the 1s peak of N (atomic concentration 2%), were found in the spectrum of PVA-coated LiCoO₂. The latter is thought to have originated from trace amounts of NMP.

The atomic concentrations of each element, measured from peak areas in the survey spectra, are listed in Table 3. Uncoated LiCoO₂ had a Co concentration of 13 atom% which has decreased to 9 atom% after the coating. In turn, the C concentration increased from 28 atom% to 38 atom% for the coated material.

The O 1s regions of all three samples are shown in Figure 11. The O 1s peak of LiCoO₂ contains at least 2 distinct components at binding energies of 531.2 and 529.1 eV. PVA showed a single oxygen peak at a higher

Table 3. Element concentrations from XPS analyses (atom%)

	LiCoO ₂	PVA	PVA-coated LiCoO ₂
C 1s	27.8	67.2	37.6
O 1s	47.1	32.5	42.4
Co 2p	12.9	–	9.3
Li 1s	12.2	–	8.2
Na 1s	–	0.2	0.5
N 1s	–	–	2.0

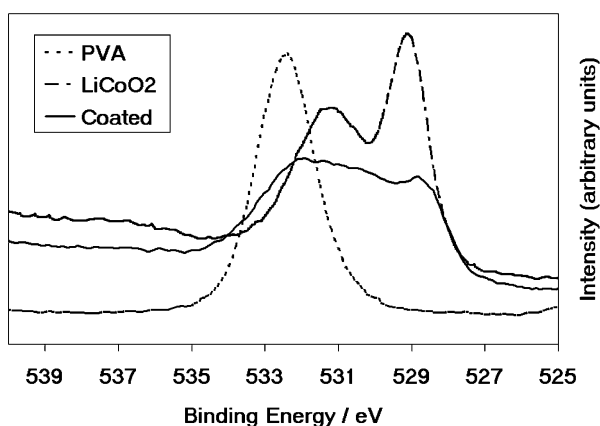


Fig. 11. O 1s regions in the XPS spectra of PVA, LiCoO₂, and PVA coated LiCoO₂.

energy of 532.6 eV. The O 1s spectrum of the PVA-coated LiCoO₂ contained a broad peak encompassing the signals from both the LiCoO₂ and the PVA.

PVA forms a soft coating and so photoelectrons may originate from deeper in the surface than for harder samples. The depth of analysis for XPS is normally 5 nm, but may be a bit more for an organic material such as PVA, as the inelastic mean free path is greater for polymers than for inorganic materials. The fact that Li and Co can still be detected on the coated sample indicates either that the coating is thinner than ca. 5 nm, or that it is not uniform.

3.4. Preparation of carbon black-coated cathode materials

LiCoO₂ was pre-treated adding 12.5 g of the oxide to 50 ml of 0.2 wt% PVA/NMP solution and stirring for 5 min. The conditioned powder was separated from the supernatant by centrifugation and washed three times with NMP to remove loose polymer. 12.5 g of PVA-conditioned LiCoO₂ were added to the carbon black dispersion and stirred for 5 min. The carbon black coated powder was separated from the supernatant by centrifugation and washed three times with NMP to remove unbound carbon black.

Thermogravimetric analysis (TGA) of the sample showed an amount of 2% carbon black after drying the sample for 2 days in vacuum.

TGA of unconditioned LiCoO₂ which had been treated with the carbon black dispersion showed that it contained less than 0.1% carbon black. Hence, only PVA-conditioned LiCoO₂ is capable of inducing coagulation.

3.5. Morphology of carbon black-coating on lithium cobalt oxide

Coated and uncoated particles of LiCoO₂ were analysed by SEM. The untreated particles of LiCoO₂ are shown in Figure 12. Carbon black-coated particles of LiCoO₂ are depicted in Figure 13. It can be seen that the carbon black coating seems quite dense and most of the oxide particles are coated completely.

3.6. Specific conductivity of carbon black-coated lithium cobalt oxide

Plain LiCoO₂ has a fairly low conductivity (Table 4). The addition of graphite increases the specific conductivity of the sample by a factor of almost 10. The specific conductivity can be further increased drastically by adding highly conductive carbon black. In one case LiCoO₂ was mixed with carbon black by stirring the components in a mortar, in the other, coated with carbon black by non-aqueous SIC. The uniform distribution of carbon black produced by the SIC coating allows a more uniform distribution of current and potential and causes an increase of the specific conductivity by a factor of 20 compared to a sample where

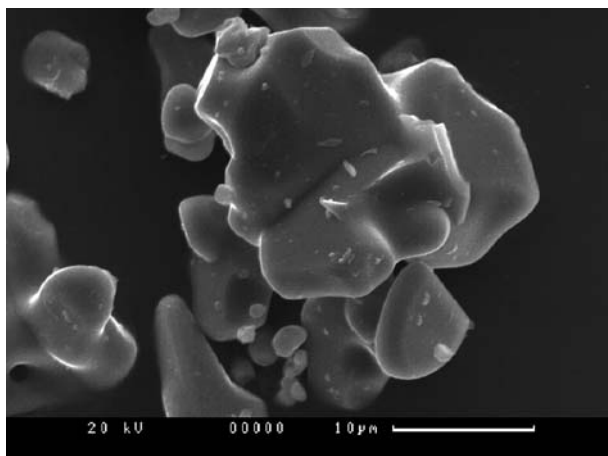


Fig. 12. SEM image of uncoated LiCoO_2 . Scale bar is $10\ \mu\text{m}$.

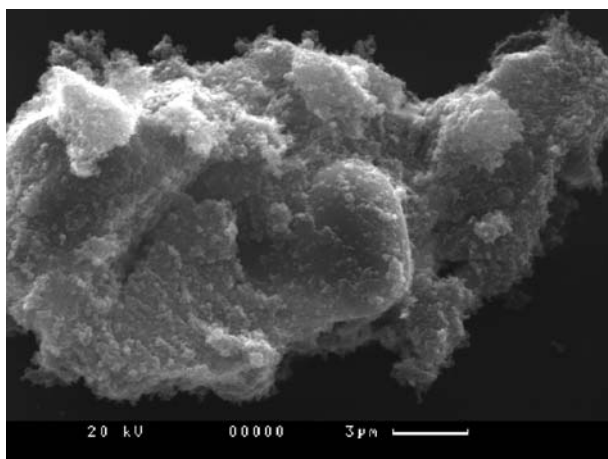


Fig. 13. SEM image of LiCoO_2 carbon-coated by non-aqueous SIC. Scale bar is $3\ \mu\text{m}$.

Table 4. Specific conductivity of various composite electrodes

Sample	Specific Conductivity/ S m^{-1}	Resistivity/ Ωm
LiCoO_2 95%	0.0666	15.01
LiCoO_2 89%, graphite 6%	0.499	2.00
LiCoO_2 89%, graphite 4%, CB 2%	14.55	0.0686
SIC- LiCoO_2 91% (89% LiCoO_2 and 2% carbon black), graphite 4%	306.3	0.00327

All samples contained 5% PTFE as a binder; CB = carbon black.

carbon black and graphite is mechanically mixed with LiCoO_2 .

4. Conclusions

N-Methyl-2-pyrrolidinone was found to be a suitable solvent for non-aqueous SIC. Carbon black in NMP needs no surfactants for stabilisation. The dispersion is stable over several weeks and requires the addition of an

electrolyte such as LiCl in order to decrease its stability for the SIC. A polyelectrolyte on a pre-treated surface leads to further destabilisation and coagulation of the dispersed particles on the surface. Polyvinylalcohol and polyvinylacetate were used as conditioners for the non-aqueous SIC method. Ellipsometry and atomic force microscopy experiments have shown that both PVA and PVAc form dense layers. Carbon black layers produced from PVA treated surfaces are more uniform than those deposited on PVAc conditioned surfaces. This is believed to be caused by the greater surface charge density of PVAc, that causes the polymer to form agglomerates.

It was shown that different types of surfaces such as mica, copper-foil and silicon wafers can be coated by non-aqueous substrate induced coagulation. Also LiCoO_2 powder, which is used as active material in Li-ion batteries can be carbon-coated by non-aqueous SIC.

Although the content of carbon black is as low as 2%, the conductivity of electrodes for Li-ion batteries made from LiCoO_2 , carbon-coated by non-aqueous SIC, remains high.

In summary, the SIC method, which up to now could only be performed in aqueous systems, has been extended to non-aqueous media. This opens up new fields of applications for materials that are sensitive to hydrolysis.

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