

Layer by layer preparation of electrodes with defined thickness by multiple use of the SIC coating process

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Abstract

By using a coating process, so-called substrate induced coagulation (SIC), thin layer electrodes of defined thickness can be prepared. After a short introduction in the process itself, first results with the electrode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are presented. Future application areas and the advantages of electrodes made by the SIC process are discussed.

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1. Introduction

Surface coating of active battery materials and of current collectors is commonly used, e.g. for decreasing contact resistances or improving self-discharge, corrosion and safety characteristics. We have developed a dip-coating process (substrate induced coagulation, SIC) resulting in self-assembling of nanoparticles on preconditioned surfaces. SIC is a method for coating surfaces uniformly with layers of nanodispersed particles (e.g. $\text{Li}_4\text{Ti}_5\text{O}_{12}$). It uses intermolecular forces between a surface pre-treated with a polymer and particles dispersed in aqueous or non-aqueous solutions [1]. The stability of the dispersion can be adjusted to a point where the interaction with the polyelectrolyte (e.g. gelatine) conditioned surface leads to coagulation of the particles in a way that they form an adhesive and rinse-proof layer on the surface (see Fig. 1).

The main driving force for the enhanced particle adsorption is believed to be the removal of stabilizing surfactant molecules from the particles by the polyelectrolyte on the substrate, inducing destabilization of the dispersion at the

substrate/solution interface and coagulation of the previously dispersed particles on the substrate surface.

For batteries, supercapacitors and fuel cells it is a trivial fact that thin electrodes exhibit better high power performance than thick electrodes. Unfortunately, it is often difficult, laborious and expensive to prepare thin electrodes of defined thickness. Here, we show how the above SIC coating technique [1] can be applied for the preparation of thin electrodes “layer by layer” from sub-micron sized powders, i.e. the thickness of the obtained electrode can be adjusted on the micron-scale.

For the first studies we focussed on spinel-type (zero-strain) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as active material [2].

2. Experimental

2.1. Material

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel was used as active material and was obtained as nanopowder from NEI Corporation (USA). The current collector of the working electrode (=substrate for the coating process) consists of a stainless steel grid with a geometric area of $10\text{ mm} \times 10\text{ mm}$. The active material was coated in the form of ultra thin films on the current collector using the SIC process [1,3–5].

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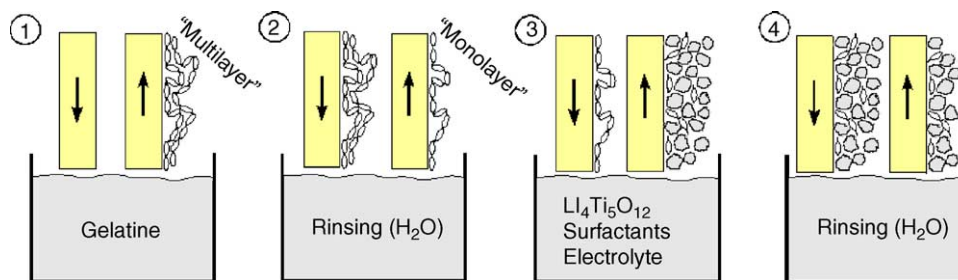


Fig. 1. Substrate induced coagulation (SIC): (1) the substrate is conditioned by dipping into a gelatine solution; (2) rinsing to remove unbound polymer; (3) dipping into a dispersion of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and (4) rinsing to remove unbound particles.

Gelatine (Fluka, type A, bloom value 180) was used as polyelectrolyte for the *conditioning bath*. Cetyltrimethylammonium bromide (Aldrich) was used as stabilizing surfactant and sodium acetate (Merck) was used as electrolyte in the *dispersion bath*. For all diluting steps deionized water was used.

For comparison, paste electrodes (=“conventionally made electrode”) have been prepared from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (NEI Corporation), graphite KS 6 (Lonza) and PVdF binder (Aldrich). The electrodes contained similar masses of active material compared to the electrodes prepared by SIC.

2.2. Preparation of electrodes

2.2.1. Conventionally made $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes

For the preparation of conventionally made electrode 91 wt% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel was mixed with 6 wt% KS6 graphite and 3 wt% of PVdF as binder for 1 h using a magnetic stirrer. Subsequently, *N*-methyl pyrrolidinone was slowly added to the resulting powder until a honey-like consistency was obtained. The slurry was further homogenized over night using a magnetic stirrer. The resulting active material was applied on the current collector with a pipette. Each electrode was pre-dried for 2 h at 120°C . Finally, the electrodes were dried under vacuum for 24 h at 120°C .

2.2.2. Electrodes made using the SIC process

As illustrated in Fig. 1, in the first step the current collector was immersed for 2 min into the *conditioning bath*. To assure that the entire surface is covered with polyelectrolyte, slightly stirring of the current collector was performed.

Subsequently, excess (=unbound) polyelectrolyte was removed by rinsing with water. Therefore, the current collector was dipped carefully two or three times into a bath of deionized water.

The conditioned current collector was immersed 2 min into the *dispersion bath* afterwards. Again carefully stirring of the conditioned current collector in the dispersion leads to a good wetting and a better coagulation of nanoparticles on the surface.

Finally, unbound particles are removed by rinsing with distilled water as mentioned above.

The SIC process was repeated four more times to obtain in total five layers of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles on the current collector

(compare Fig. 2). It should be pointed out that this electrode does not contain any conducting additive like, e.g. carbon or graphite.

2.3. Preparation of the conditioning bath

Gelatine was dissolved in distilled water at a temperature of 60°C to receive an aqueous solution of 0.2 wt% polyelectrolyte. The pH of the gelatine-containing solution was adjusted with aqueous 0.1 M KOH to a value of pH 8.90.

2.4. Preparation of the metastable dispersion bath

0.66 g cetyltrimethylammonium bromide was dissolved at room temperature in 100 mL distilled water. 1.00 g of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, was added and dispersed for 10 min using a turbo mixer (13,000 rpm). Subsequently, 0.41 g NaOAc were added and dissolved. The dispersion was ultrasonicated for 15 min prior to use.

2.5. Electrochemical techniques and instrumental details

Cyclic voltammograms (CVs) were recorded with an Adesys Electrochemical Research Station Model 1612 in a potential range of 1000 to 2000 mV versus Li/Li^+ . Cyclic voltammetry experiments started at open circuit potential (OCP). The measurements were carried out at room temperature ($25 \pm 2^\circ\text{C}$) in a glove box containing an argon atmosphere.

Constant current charge- and discharge-cycling was performed with the same equipment as mentioned above in the

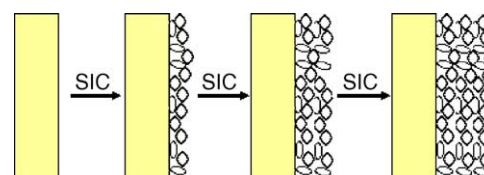


Fig. 2. Stepwise preparation of a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode using the SIC process. Each coating step creates layers of sub-micron to micron thickness, i.e. the thickness of each layer is approximately in the range of the size of the particles.

same potential range. For cycling, the current was set to 0.1, 1.0, 10.0 and 40.0 C-rate, respectively. Charge and discharge correspond to the lithiation and de-lithiation process of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode, respectively.

3. Results and discussion

The stepwise preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes using the SIC process leads to mechanically very stable electrodes. Each coating step creates layers of sub-micron to micron thickness, i.e. the thickness of each layer was approximately in the range of the size of the particles.

The CVs of electrodes containing $\text{Li}_4\text{Ti}_5\text{O}_{12}$, either prepared according to the SIC process or conventionally made are compared in Fig. 3. Both electrodes show a chemically reversible peak pair at 1.55 V versus Li/Li^+ . The SIC electrode, however, exhibits obviously better kinetics indicated by a sharper pair of peaks and a smaller difference between the anodic and cathodic peak potential.

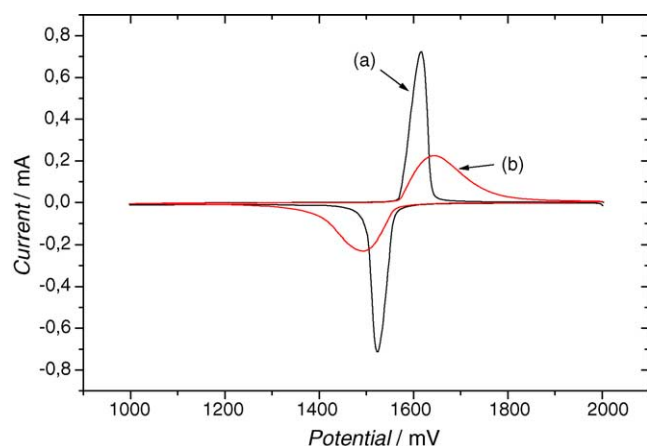


Fig. 3. CVs ($v = 50 \mu\text{V s}^{-1}$) of differently prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes. The electrode made by SIC (a) exhibits better performance than the conventional paste electrode (b). Electrolyte: 1 M LiClO_4 in EC:DEC (1:1).

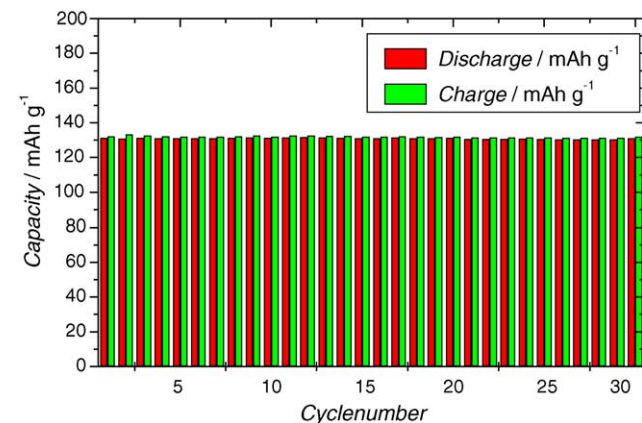


Fig. 4. Charge/discharge capacities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode made using the SIC process at 0.1 C-rate. Electrolyte: 1 M LiClO_4 in EC:DEC (1:1).

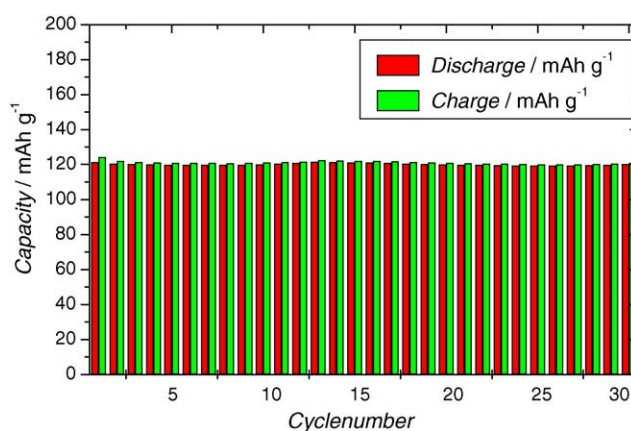


Fig. 5. Charge/discharge capacities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode made using the SIC process at 1.0 C-rate. Electrolyte: 1 M LiClO_4 in EC:DEC (1:1).

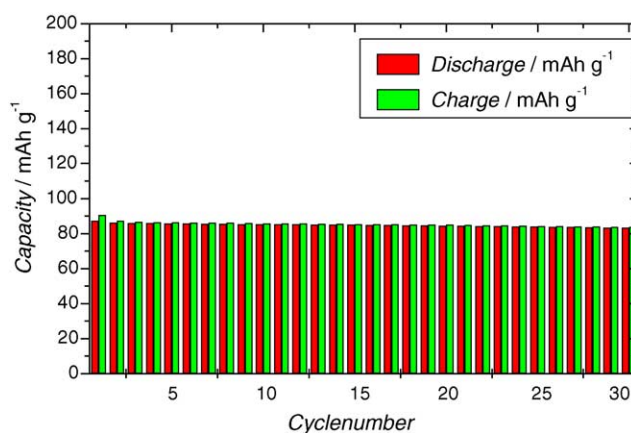


Fig. 6. Charge/discharge capacities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode made using the SIC process at 10 C-rate. Electrolyte: 1 M LiClO_4 in EC:DEC (1:1).

Constant current cycling tests confirm the good performance of the electrode made by SIC at various C-rates as demonstrated in Figs. 4–7, the capacity of the electrode made by SIC was found to be close to 132 mAh g^{-1} (Fig. 4).

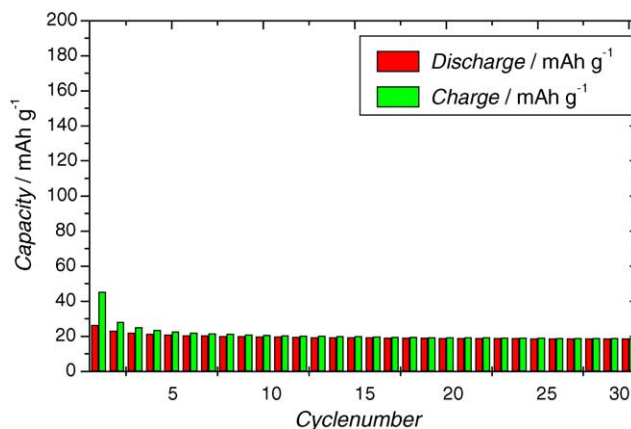


Fig. 7. Charge/discharge capacities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode made using the SIC process at 40.0 C-rate. Electrolyte: 1 M LiClO_4 in EC:DEC (1:1).

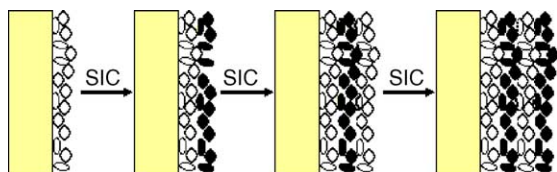


Fig. 8. Principle of SIC composite coating process with different coating materials during the coating sequence.

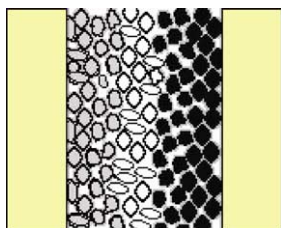


Fig. 9. Principle of thin sandwich type electrochemical cell made using the SIC process. Grey particles: anode material; white particles: separator material; black particles: cathode material.

4. Conclusion and outlook

The SIC coating process has numerous applications. Here, we could show that the SIC process is very suitable to obtain thin mechanically stable $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes of defined thickness. The method yields electrodes with better electrochemical performance than conventional electrodes, even when no carbon as conductive additive is present the electrode.

We believe that the thin film preparation via the SIC process is not only an appropriate process for creation of battery electrodes but might be extended to fuel cells and supercapacitors [5]. There should be even many applications beyond the topic electrochemical power sources. With regard to electrochemical power sources, apart from the above mentioned fea-

tures, three further main advantages of the SIC process shall be finally mentioned: (i) Apart from the small polyelectrolyte, e.g. gelatine amount, SIC made electrode basically contain no binder, but are still mechanically stable. This ensures beneficial prerequisites for good electronic contact between the particles and a good contact interface with the electrolyte. (ii) The coating material for the SIC multi-step coating process can be changed during the coating sequence that multilayer electrode with different properties can be created (Fig. 8). By doing this, layers with certain function and /or composition can be brought together, e.g. polar layers and less polar layers as needed for fuel cell electrodes. Also the fabrication of electrodes showing an alternation of conductive and less conductive layers can be possible by such a measure. (iii) At last, even complete (thin film) “sandwich-type” electrochemical cells may be possible, as depicted in Fig. 9.

Acknowledgments

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