Journal of Power Sources 348 (2017) 130–137

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

3D indium tin oxide electrodes by ultrasonic spray deposition for current collection applications

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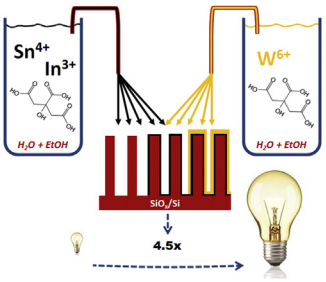
HIGHLIGHTS

- 3D ITO electrodes prepared with a low cost, highly-up scalable method.
- Various 3D structures were coated, showing versatility of the approach.
- The conductivity was studied with vdPauw and electrochemical methods.
- Deposition of WO_3 on top of 3D ITO shows a large capacity enhancement.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 December 2016
Received in revised form
22 February 2017
Accepted 1 March 2017

Keywords:
ITO
Films
Current collector
3D structures
TCO
Transparent conductive oxide

ABSTRACT

Three dimensionally (3D) structured indium tin oxide (ITO) thin films are synthesized and characterized as a 3D electrode material for current collection applications. Using metal citrate chemistry in combination with ultrasonic spray deposition, a low cost wet-chemical method has been developed to achieve conformal ITO coatings on non-planar scaffolds. Although there is room for improvement with respect to the resistivity ($9.9 \cdot 10^{-3}$ Ω·cm, 220 nm thick planar films), high quality 3D structured coatings were shown to exhibit conductive properties based on ferrocene reactivity. In view of applications in Li-ion batteries, the electrochemical stability of the current collector was investigated, indicating that stability is guaranteed for voltages of 1.5 V and up (vs. Li^+/Li). In addition, subsequent 3D coating of the ITO with WO_3 as a negative electrode (battery) material confirmed the 3D ITO layer functions as a proper current collector. Using this approach, an over 4-fold capacity increase was booked for 3D structured WO_3 in comparison to planar samples, confirming the current collecting capabilities of the 3D ITO coating. Therefore, the 3D ITO presented is considered as a highly interesting material for 3D battery applications and beyond.

1. Introduction

In a world seeking a sustainable future, smart materials and structures are opted for energy harvesting, storage and consuming

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http://dx.doi.org/10.1016/j.jpowsour.2017.03.006
0378-7753/

applications. 3D structure enhancements are often applied to enhance active material performance, mostly based on a kinetic advantage due to a better current distribution per (active) material volume. Examples of this technology can be found within the field of hydrogen technology [1], 3D supercapacitors [2], PV applications [3], 3D lighting (LEDs) [4,5] and battery technology [6,7]. For 3D LED applications, based on the enlargement of active surface area for light generation, 3D structured transparent conductive oxides (TCO's) can contribute to highly efficient 3D LEDs [4]. Upon successful implementation of such a 3D electrode, further improvement of these devices would be possible as these systems currently lack a transparent, 3D structured electrode as top contact for the GaN pillar structures [5]. For 3D Li-ion batteries, or more specifically '3D integrated all-solid-state Li-ion batteries' [7,8], 3D structured electrodes (or also referred to as 'current-collectors' in this field) are essential for transportation of electrons to the active battery materials. 3D all-solid-state Li-ion batteries combine the benefits of an all-solid state battery, namely increased lifetime, enhanced safety and miniaturization - with a significant improvement in capacity due to 3D architectures [6,7,9]. As all these applications involve the exchange of electrons; suitable electrode materials are required, acting as current collectors for 3D structured (energy) materials. Although several examples of 3D structured metals and doped semi-conductors are available [10–12], conductive coatings resistant to high temperatures are rare. Various reports have been made for 3D metallic foams, consisting of porous (metallic) Cu or Ni. Although corrosion of these metals can be utilized to form active battery materials directly on the current collector [13,14], both structure and required synthesis temperature of (ceramic) electrode materials such as $Li_4Ti_5O_{12}$ and $LiCoO_2$ render this approach unsuitable for 3D thin film all-solid-state Li-ion batteries [11,15,16]. Currently, the choice of 3D structured thin film current collectors is primarily limited to ALD grown titanium nitride (TiN) [17,18] and platinum (Pt) [19,20]. More specifically, TiN is an excellent choice as a current collecting electrode for 3D Li-ion battery applications, as the material acts as a current collector and buffer layer to prevent lithium diffusion into the 3D structured support [18]. Although both TiN and Pt exhibit superior conductivity, the vacuum conditions of the costly deposition method limits upscaling possibilities. Moreover, TiN tends to oxidize and forms poorly conducting TiO_2 under oxidative annealing conditions [21]. Hence, emerging 3D structured technologies requiring elevated annealing temperatures are limited by the lack of choice of suitable 3D structured electrode materials [22]. Besides metals and nitrides, Transparent Conductive Oxides (TCOs) are also considered as current collectors for various applications. Using ALD, conformal coatings of aluminium doped zinc oxide (AZO) and indium tin oxide (ITO) have been reported [23,24]. However, as stated previously, ALD is a costly route. Via chemical bath deposition, zinc oxide (ZnO) was deposited in trenches, though the aspect ratios achieved were below unity [25]. Within this study, the deposition and function of ITO as an electrode material for current collecting applications is investigated by using a wet-chemical route with a huge upscaling potential. Being an oxide, concessions have to be made with respect to the resistivity, while comparing this material with metallic conductors. Needless to say, the crystallinity and occurrence of vacancies is influenced by annealing, hence the conductivity of ITO is susceptible to (high temperature) annealing conditions dictated by a second material in case stacking is attempted (in view of device integration). However, oxidation issues (a major issue for the TiN previously mentioned) cannot occur as the ions involved are already in the highest oxidation state (In^{3+} and Sn^{4+}). Therefore, the 3D structured ITO films are an interesting candidate to serve as potentially high temperature resistant current collectors for (3D) thin film Li-ion batteries.

Recently, Gielis et al. developed a process to deposit oxide materials on non-planar surfaces with high aspect ratios, using a tailored wet-chemical approach in combination with ultrasonic spray deposition [22,26]. In this approach, a stable (metal-citrate) precursor is atomized via vibrations at ultrasonic frequency, yielding a fixed droplet size distribution, where the average size of the droplets leaving the nozzle is approximately 8 μm [27]. Due to evaporation, the droplets are even smaller when they hit the substrate [28]. This possibly enables the deposition of 3D structured TCO materials, to act as current collecting electrodes in various applications. In this study, the current collecting capabilities of ITO were studied in view of application in 3D Li-ion batteries. In addition, the ITO was coated with a negative electrode material for Li-ion batteries as a proof-of-principle. WO_3 was chosen for this purpose, because of (i) the relatively high volumetric energy density and stable cycling behavior (640 $mAh \cdot cm^{-3}$) [29], (ii) the compatibility with relatively unstable solid electrolytes, such as Perovskite $Li_{0.35}La_{0.55}TiO_3$ [29] and (iii) the possibility to deposit this material on 3D scaffolds by ultrasonic spray deposition [22].

2. Experimental

An aqueous citrato peroxo Sn^{4+} solution was prepared according to the synthesis route developed by Stanulis et al. [30]. Hydrogen peroxide (H_2O_2, Acros Organics, 35%) was added to tin oxalate (Sigma Aldrich, 98%) in a 12:1 M ratio and heated to 80 °C. Next, citric acid (CA, Sigma Aldrich, ≥99%) was added in a 6:1 M ratio with respect to Sn and heated to 80 °C. Finally, the pH was raised to 7.0 with ammonia (NH_3, Merck, 32%) to obtain the aqueous Sn^{4+} precursor, with a colorless, transparent appearance. In^{3+} citrate was prepared by mixing indium hydroxide ($In(OH)_3$, Umicore electro-optic materials) and CA in a 1:4 M ratio, followed by the addition of water. This mixture was heated under reflux conditions for 90 min at 120 °C. After cooling, the pH was adjusted to 7.0 with ammonia, yielding a transparent colorless solution. For both Sn^{4+}- and In^{3+}-solutions, the excess of CA was required to prevent precipitations. The concentrations of both precursors were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 3300, PerkinElmer). Next, the aqueous Sn^{4+}- and In^{3+}-solutions were mixed in a 1:9 M ratio. Finally, ethanol was added to the aqueous precursor in a 9:10 volumetric ratio, as proposed by Gielis et al. [22,26]. The total metal-ion concentration of the final mixed precursor amounted to 10 mM.

Three different types of substrates were used for this study: (i) planar Si wafers with 200 nm thermal oxide (imec, Heverlee, Belgium), (ii) planar Si wafers with 1–2 nm native oxide (imec, Heverlee, Belgium), (iii) Si micro-cylinders of 50 μm in length, 1.5 μm radius with an inter-cylinder distance of 5 μm, prepared by reactive ion etching (imec, Belgium), further referred to as 'Si micro-cylinders' and (iv) trench structured Si wafers, prepared by reactive ion etching (Philips, Eindhoven, the Netherlands) further referred to as 'trenches'. All the substrates were submitted to a cleaning procedure, either by applying a UV/O_3 treatment (30 min at 60 °C) or a modified piranha cleaning procedure. The latter consisted of a consecutive sulphuric acid-peroxide and ammonia-peroxide (SPM/APM) treatment [31]. Tungsten oxide was deposited consecutively on top of the ITO coated substrates, as reported earlier [22].

The mixed precursor was deposited on various substrates via ultrasonic spray deposition (Exacta Coat, Sono-Tek cooperation) with set deposition temperatures ranging from 170 °C to 230 °C. The liquid was dispensed at 0.2 ml min^{-1} and the N_2 carrier gas pressure was set at 1.5 psi. The distance of the spray nozzle to the substrate was approximately 2.7 cm and it moved with a speed of 100 mm s^{-1}. The number of deposition cycles (i.e. the number of