CrossMark
click for updatesCite this: *RSC Adv.*, 2016, 6, 51747

From liquid to thin film: colloidal suspensions for tungsten oxide as an electrode material for Li-ion batteries†

E. J. van den Ham,^{*a} K. Elen,^a I. Kokal,^b B. Yağci,^c N. Peys,^a G. Bonneux,^a F. Ulu,^a W. Marchal,^a M. K. Van Bael^a and A. Hardy^a

Using a colloidal suspension, tungsten oxide thin films (150 nm) have been prepared *via* ultrasonic spray deposition using two different current collectors, namely TiN and Pt. First, the precursor chemistry was studied, revealing that the tungsten present is reduced due to the formation of chlorine gas. Due to a dehydrogenation 1,1-diethoxyethane (DEE) and hydrogen chloride (HCl) evolve from the precursor, reducing the chloride content of the precursor. The thin films were annealed at 400 and 500 °C, yielding tetragonal tungsten oxide without the presence of chlorides. Electrochemical analysis indicated that the TiN current collector has a pronounced positive effect on cycling behavior of the WO₃ thin film. A higher annealing temperature yields an improved performance, but annealing at temperatures as low as 400 °C also yielded electrochemically active WO₃. The current study presents a versatile method to produce electrochemically active tungsten oxide thin films with a high volumetric capacity (640 mA h cm⁻³) at relatively low temperature to be applied in all-solid-state Li-ion batteries.

Received 5th April 2016

Accepted 20th May 2016

DOI: 10.1039/c6ra08769h

www.rsc.org/advances

Introduction

In a world seeking a sustainable future, batteries are expected to play a big role regarding energy storage for mobile applications. However, the current generation of Li-ion batteries with liquid electrolytes suffers from several issues, including safety hazards and capacity fading.^{1–3} One of the known approaches is the concept of thin film all-solid-state Li-ion batteries, limiting the thickness of both the electrolyte and electrodes to prevent high resistances.^{2,4} In this way, the big advantages of solid electrolytes can be utilized, namely increased lifetime, improved safety and a broader operating temperature window.^{1,2,5}

Various thin film electrode materials, such as Li₄Ti₅O₁₂ (LTO),^{6,7} LiMn₂O₄ (LMO)⁶ and WO₃,⁸ have been investigated. Traditionally, WO₃ is a material known for its catalytic capabilities.^{9,10} Besides lithium,^{8,11–13} other alkali ions can be inserted into its crystal structure.¹³ This property makes WO₃ the basis of smart windows, based on its electrochromic properties.^{13–19} Although various reports indicate the

superiority of LTO as an oxide based negative electrode according to its higher energy density, the WO₃ outclasses the LTO according to its volumetric capacity 604 (ref. 20) *vs.* 228 mA h cm⁻³ (ref. 21 and 22). The volumetric capacity is more applicable for thin film all-solid-state Li-ion batteries since the total battery consists of scaffolding material, current collectors and electrolyte.

In addition, the relative high (de)intercalation voltage between 1.5 and 3 V (*vs.* Li⁺/Li)^{8,11,13} proves to be very useful when combining WO₃ with a solid electrolyte. Indeed, one of the main challenges of the thin film all-solid-state Li-ion batteries^{22,23} is the incorporation of a solid electrolyte. Besides LiPON,^{24,25} Li-ion conducting silicates^{26,27} and few a garnets;^{28–30} thin film solid electrolytes have a limited electrochemical stability at low voltages.^{1,31} Thus the high voltage WO₃ negative electrode opens up a broader range of applicable solid electrolyte materials such as perovskite Li_{3x}La_{(2/3)–2x}TiO₃ (LLT)^{32–36} and titanium-containing NASICON.^{37,38}

Finally, titanium nitride (TiN) is opted as an alternative for the rare and expensive Pt current collector^{25,34} since it combines good electronic conductivity with Li-ion blocking properties.³⁹ Unfortunately, TiN tends to oxidize under oxidative annealing conditions.⁴⁰ Here, the potentially low annealing temperature needed for the realization of crystalline WO₃ at 300 °C (ref. 15 and 41) prevents TiN oxidation and enables its use as a current collector.

In summary, WO₃ is a promising negative electrode worth studying in detail. The current research employs chemical

^aHasselt University, Institute for Materials Research, Inorganic and Physical Chemistry and IMEC, Division IMOMEC, Martelarenlaan 42, 3500 Hasselt, Belgium. E-mail: jonathan.vandenham@uhasselt.be

^bPavezyum Chemicals, Orhanlı Mah. Ulu Sokak No. 3, 34956 Tuzla, Istanbul, Turkey

^cKoç University Surface Science and Technology Center (KUYTAM), Rumelifeneri Yolu, Sariyer, 34450, Istanbul, Turkey

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra08769h

solution deposition^{15,17,19,42} to study WO₃ as a potential negative electrode material for all-solid-state Li-ion batteries.

Experimental

Synthesis of the chlorine-based tungsten precursor

Tungsten chloride (WCl₆, Sigma Aldrich, 99.9%) was dissolved in ethanol (ethanol absolute, VWR) and stirred for a 20 minutes, yielding a transparent yellow liquid. Next, water was added until a 1 : 1 water to ethanol volumetric ratio was obtained similar Regragui *et al.*,¹⁵ resulting in a transparent dark blue liquid (*cf.* Video S1†). The final tungsten concentration in the water/ethanol solution amounted 10 mM.

Deposition on substrates

TiN (Si coated with 60 nm of CVD TiN) and Pt (the TiN with an additional 100 nm sputtered Pt) substrates were used in this study. Both substrate types were treated by UV/O₃ (60 °C, 30 min, Novascan PSD Pro Series) prior to the deposition. The precursor solution was deposited onto the substrates *via* ultrasonic spray deposition (Exacta Coat, Sono-Tek cooperation) using the Accumist nozzle (Sono-Tek cooperation). The deposition temperatures were set at 150, 200 and 250 °C. The precursor was dispensed at 0.5 mL min⁻¹ and the N₂ carrier gas pressure was set at 1.5 psi. The spray nozzle was located 6.9 cm above the substrate and moved with a speed of 100 mm s⁻¹. The spray cycle was repeated 10 times with a waiting time of 5 seconds. After deposition, a sequential hot plate treatment, in static air, was carried out at 300 °C (2 min) and at 400 or 500 °C (1 hour). Both WO₃/TiN and WO₃/Pt samples received the same thermal treatments and were all stored in an Ar-filled glovebox after the post-deposition anneal.

Characterization – liquid phase

Ultraviolet-visible spectroscopy was performed on precursor solutions with 1 mm of tungsten by a Amersham Biosciences Ultrospec 100 pro tool. A Tyndall experiment was performed on the tungsten precursor (1 mm) using a 35 mW diode laser (NanoBrook 90Plus). GC-MS was performed on the headspace of the preheated (10 min, 70 °C) precursor solution *via* a Thermo Scientific Trace 1310 GC using a DB5-MS capillary (length 30 m, diameter 0.25 mm and filter size 0.25 µm); coupled with a Thermo Scientific ISQ LT MS, scanning between 33 and 350 u every 0.2 seconds.

Characterizations – powders

The thermal decomposition profile of the precursor powder, obtained by drying of the precursor solution at 60 °C, was investigated by thermogravimetric analysis coupled with mass spectroscopy detector (TG-MS, TA instruments Q5000 with Pfeiffer quadrupole MS). 6 mg of the powder was heated in a Pt sample pan, ramped at 10 °C min⁻¹ from room temperature to 500 °C in dry air (25 mL min⁻¹) and a N₂ balance gas (10 mL min⁻¹).

The crystallization process of the precursor powder was studied by high-temperature X-ray diffraction (HT-XRD, Bruker

D8 with an Anton Paar HTK1200 high temperature chamber) from 250 to 900 °C (10 °C min⁻¹), in steps of 50 °C with a counting time of 52.8 s per step. Transmission electron microscopy (TEM) was performed on a FEI Technai G2 Spirit Twin, operated at 120 kV. For this purpose, the precursor solution was sonicated for 2 minutes, small drops were casted onto a carbon coated copper grid (EMS, FCF-200-Cu) and dried under an infrared lamp for 20 minutes.

Characterizations – films

The morphology of annealed tungsten oxide films was investigated *via* scanning electron microscopy (SEM, FEI Quanta 200F). The thickness of the films was determined *via* SEM cross sections, coupled with the density of WO₃ (7.15 g cm⁻³) the total amount of deposited WO₃ could be determined. The composition of the film was probed by XPS *via* a Thermo Scientific K-Alpha spectrometer using an aluminum anode (Al Kα = 1468.3 eV) at an electron take-off angle of 90° (between the sample surface and the axis of the analyzer lens). The depth-profiling experiment was effected by bombarding 1.000 eV Ar⁺ ions for 6 levels of 60 s etching rate. The spectra were recorded using an Advantage 5.9 data system. The binding energy scale was calibrated by assigning the C 1s signal at 284.5 eV. Cyclic voltammetry and charge/discharge measurements were performed with an Autolab PGSTAT128N, using a three electrode setup with a custom made Teflon cell similar to the setup used by Notten *et al.*³⁹ The WO₃/TiN and WO₃/Pt samples were used as the working electrode *via* a copper disc connected to the back of the substrate. Silver paint (Belelux scientific) was used to ensure good conductivity between the copper disc and the substrate. The top of the substrate was accessible to the liquid electrolyte (1.0 M LiClO₄ dissolved in polycarbonate, Soulbrian MA) and a Kapton® O-ring was used for sealing. Metallic lithium (99.9% Sigma Aldrich) served as the counter and reference electrodes. After 3 cycles of CV at 1 mV s⁻¹ between 1.5 and 4.0 V, charge/discharge measurements were performed between the same cut-off voltages with a constant current of 10 µA (1C). The test cell was operated at 20.0 °C *via* a custom made temperature control chamber, inside an Ar-filled glovebox with water an oxygen concentrations <1 ppm. The crystallinity of the films was investigated by XRD *via* a Bruker D8 equipped with a Lynx eye detector, using a step size of 0.040° and a counting time of 3 seconds per step at room temperature. *Ex situ*, post-cycling XRD analysis were performed after 100 cycles for both WO₃/TiN and WO₃/Pt samples. After removal from the electrochemical cell, the samples were rinsed with ethanol to remove the organic electrolyte and immediately measured using the stated XRD setup under ambient conditions.

Results and discussion

Precursor chemistry

Precursor analysis – the liquid phase. Dissolution of tungsten chloride (WCl₆) in ethanol leads to a transparent, yellow solution, although the yellow color decays over time. After

a few days a greenish precipitation was observed. Fig. 1 (red curve) shows that a significant absorption band is present in the UV-A region. The onset of this band is situated on the edge of the visible spectrum, hence the solution exhibits a yellow color. Based on the sample composition and location of the band, it is assigned to dissolved chlorine gas (Cl_2).^{41,43–46} Fig. 1 shows that the absorption of this band decreases as a function of time. Indeed, after 90 minutes a colorless liquid is observed. This indicates that the majority of the Cl_2 has left the precursor during the first 90 minutes after synthesis. By adding water, a dark blue, transparent liquid is observed and the UV-Vis spectrum shows a significant absorption band between 600 and 780 nm (Fig. 1). This suggests the reduction of W^{6+} (ref. 47) and/or forming WO_x agglomerates. Besides light absorption, light scattering of the precursor was observed with a simple Tyndall experiment. This implies that particles are present in the liquid. Fig. 2 shows a TEM image of these particles and indicated the presence of two types of particles: large rod-like particles with 100–150 nm length (Fig. 1) and small circular particles of 20 nm (Fig. S3†). Therefore, it is assumed that the blue coloration is caused by tungsten oxide agglomerates. This blue color can directly be related to polaron transitions between $\text{W}^{6+}/\text{W}^{5+}$ or $\text{W}^{5+}/\text{W}^{4+}$,^{48–50} or by a bipolaronic transaction based on $\text{W}^{6+}/\text{W}^{4+}$.⁵¹ This supports the statement that W^{6+} is reduced in the solution. Note that the rod-like particles are crystalline, as indicated by the electron diffraction (ED) (Fig. 2, inset).

Headspace GC-MS measurements (Table 1) indicate that hydrochloric acid (HCl) evolves during the dissolution of the tungsten chloride by the presence of a large intensity peak at a retention time of 1.30 minutes. The GC-MS results do not indicate the evolution of Cl_2 directly. However, 1,1-diethoxyethane (DEE) was observed at a retention time of 3.66 minutes (Table 1). Assuming that (i) the Cl_2 instantaneously reacts with the ethanol matrix, forming acetaldehyde, and (ii) the acetaldehyde instantaneously reacts with the ethanol matrix forming

Fig. 1 UV/VIS spectrum of 1 mM WCl_6 precursors in ethanol and ethanol/water (1 : 1) solutions.

Fig. 2 TEM image of the tungsten precursor deposited on a copper grid and dried before measuring. The inset shows electron diffraction (ED) of a cluster of rod-like particles.

Table 1 Summary of the headspace GCMS results for WCl_6 dissolved in ethanol only, as well as the ethanol/water mixture. Details can be found in Fig. S1 and S2

Product	Retention time [min] ethanol/trace water	Retention time [min] ethanol/water 1 : 1 ratio
HCl	1.28	1.30
DEE	3.67	3.66

DEE;^{52,53} the observed DEE is explained. The hydrochloric acid, originating from the WCl_6 dissolution, fulfills the acidic condition known to catalyze the latter reaction at room temperature.^{53,54}

In summary, the following reaction mechanism is proposed:

(i) Chloro-alkoxide substitution shown in eqn (1):⁴¹

(ii) Cl_2 formation shown in eqn (2):⁴⁴

(iii) Dehydrogenation of ethanol shown in eqn (3):⁴⁴

(iv) Reaction between acetaldehyde and ethanol to DEE shown in eqn (4):^{53,54}

Fig. 3 HT-XRD of dried precursor powder, at various temperatures (indicated) in static air.

Precursor analysis – towards oxide formation. The X-ray diffraction of the dried precursor, without any further thermal treatment (Fig. 3), already indicates the presence of the hydrogen tungsten oxide hydrate ($\text{H}_{0.12}\text{WO}_3 \cdot 2\text{H}_2\text{O}$, PDF# 40-0693). The presence of this crystal phase supports the (partial) W^{6+} reduction hypothesis, explaining the blue color of the colloid suspension and of the prepared precursor powder.

Since TEM-ED (Fig. 2, inset and S3,† inset) indicates that only the rod-like particles are crystalline, this crystal phase is assigned to the rod-like particles. This crystalline phase can only be formed by (i) hydrolysis of ethoxy groups into hydroxy groups and (ii) by condensation of the formed hydroxy group with another hydroxy or ethoxy group into an oxygen bridge between two tungsten ions.^{55,56}

Heating the dried precursor powder reveals a transition to monoclinic WO_3 (PDF# 24-0747) already at 300 °C in Fig. 3. Though a shift of XRD peaks to lower 2θ values is expected based on thermal expansion (e.g. the (112) peak of the orthorhombic phase at 28.0°), a more pronounced shift is observed for the (222) and (400) peaks of the monoclinic phase, at 41.9 and 50.0° respectively. This indicates a phase transition from the monoclinic to orthorhombic WO_3 (PDF# 1-71-0131). Although both phases are difficult to differentiate, this temperature-dependent phase transition was reported previously in detail.^{57,58}

To further study the changes occurring during heating, TG-MS was carried out on the dried precursor (Fig. 4). The MS only indicates the evolution of water: OH^+ ($m/z = 17$) and H_2O^+

($m/z = 18$). This evolution is separated in two steps: around 65 and 225 °C. Combined with the results gained from the HT-XRD (Fig. 3), the first weight loss at 65 °C is attributed to evaporation of residual (free) water. The second weight loss at 225 °C is assigned to the release of crystal water. The last step only accounts for 6 wt% of the total weight loss, revealing that the majority of the sample contains amorphous phases. A fully crystallized sample (i.e. $\text{H}_{0.12}\text{WO}_3 \cdot 2\text{H}_2\text{O}$) would lead to the removal of crystal water with a weight loss of approximately 13 wt%.

Since no evolution of chlorides is found during the thermal treatment, the hypothesis that the chlorides leave the system during precursor synthesis is further confirmed. The total weight loss of 8 wt% during the thermal treatment up to 500 °C is a beneficial precursor property regarding film formation since less shrinkage and densification is to be expected leading to less cracks in the final film.⁵⁹

In summary the following insights regarding the tungsten precursor chemistry are obtained:

- (1) A part of the W^{6+} originating from the WCl_6 source is reduced to W^{5+} or W^{4+} via the evolution of HCl and DEE from the liquid phase;
- (2) Water causes hydrolysis and condensation reactions leading to a colloidal suspension containing crystalline particles;
- (3) The precursor powder releases a very small amount of water (8 wt%) during thermal treatment which will be beneficial for the film formation.

Fig. 4 TGA-MS of dried tungsten precursor, during heating to 500 °C at 10 °C min⁻¹ in dry air.

Fig. 5 SEM images of WO₃ coated TiN substrate. Top view images are shown for (a) TiN at 150 °C, (b) TiN at 200 °C. A cross section using back-scattered imaging is shown in (c) for TiN at 150 °C. All samples were annealed at 500 °C in static air after deposition.

Tungsten oxide thin films

Film morphology. (Cross-sectional) SEM was used to visualize the films' morphology and thickness (Fig. 5). Whereas the surface of the thin film deposited at 150 °C is relatively smooth (Fig. 5a and c), the surface looks rather rough while increasing the deposition temperature to 200 °C (Fig. 4b). After the deposition at 250 °C, no material is present on the substrate (not shown). These observations are in agreement with the film formation mechanism proposed by Perednis *et al.*⁶⁰ As the deposition temperature increases, the size of precursor droplets decreases due to an increased solvent evaporation. In an extreme case (here 250 °C), the droplets are converted to

powders before hitting the substrate, resulting in the deposition of particles with a poor substrate adhesion.

However, this film formation mechanism does not explain the difference in morphology as observed between the deposition temperatures of 150 and 200 °C, respectively resulting in a smooth or rough surface. It is proposed that a lower deposition temperature (*i.e.* 150 °C) leads to a lower solvent evaporation rate allowing for coalescence⁶¹ to occur for the particles present in the sprayed suspension after hitting the substrate surface, hence leading to a smooth surface. Here, 10 deposition cycles result in a film thickness of about 150 nm (Fig. 5c). A higher deposition temperature (200 °C) causes a fast solvent evaporating inhibiting particle coalescence and leading the root-like surface morphology.

Film composition and phase formation. As discussed previously, the precursor study indicated that most of the chlorides are leaving the precursor in the liquid phase. This is confirmed by XPS measurements performed on thin films, which do not show any signs of chlorides (*cf.* Fig. S8 and S9†). Regarding the oxidation state of tungsten, the XPS spectrum of W 4f (1a) resulted in doublets of 4f_{7/2} at 37.6 eV and 4f_{5/2} at 35.2 eV (Fig. 6). These energy positions correspond to the valence state of W⁶⁺.^{15,62,63} This implies that the oxidative anneal applied after deposition oxidizes the W⁵⁺ present in the precursor. Finally, the XPS spectrum of O 1s (Fig. S6†) with a binding energy at 530.3 eV was assigned to O²⁻ that form strong W–O bonds.⁶⁴ No difference in film composition was found while changing the substrate from TiN to Pt (*cf.* Fig. S4–S9†). To probe more than just the top, surface etching was performed. As was the case for the top surface, no chlorides were detected deeper inside of the layer (Fig. S8†). However, due

Fig. 6 W 4f XPS spectrum of WO₃ films annealed at 500 °C for 1 hour (static air) on TiN.

to the fact that Ar⁺ was used for etching, no conclusions could be drawn regarding the oxidation state of the tungsten present (Fig. S4†). It is known that a high energy etching tool, Ar⁺ etching reduces metal ions, especially in case of tungsten.^{48,65}

Although the XPS measurements regarding tungsten were restricted to surface analysis, cyclic voltammetry (CV), probing a larger volume of the WO₃ films, also confirmed the presence of W⁶⁺ (Fig. 7), as W⁶⁺ and W⁵⁺ can be discriminated based on their reduction potentials.^{51,66} A first reduction peak at 2.67 V can be related to the reduction of W⁶⁺ to W⁵⁺ (indicated by 1 in Fig. 7), the second reduction at 2.38 V corresponds to the consecutive W⁵⁺ to W⁴⁺ reduction⁵¹ (indicated by 2 in Fig. 7). In accordance with XPS, cyclic voltammetry confirms that W⁶⁺ is

Fig. 7 Cyclic voltammogram of 10 layers of WO₃ deposited on TiN (black) and Pt (red), measured at 1 mV s^{−1} in 1 M LiClO₄ in PC. The films were submitted to a post deposition anneal of 1 hour at 500 °C in static air. The numbers indicate the reduction and oxidation reactions occurring: (1) W⁶⁺ → W⁵⁺, (2) W⁵⁺ → W⁴⁺, (3) W⁴⁺ → W⁵⁺ and (4) W⁵⁺ → W⁶⁺.

present in the films. The fact that the W⁵⁺ to W⁴⁺ reduction occurs does not mean W⁵⁺ is present in the pristine film as this reaction takes place after the W⁶⁺ to W⁵⁺ reduction, yielding an overall W⁶⁺ to W⁴⁺ reduction.

XRD measurements on the films deposited on the two different substrates both indicate the presence of tetragonal WO₃ phase (Fig. 8, bottom), for which W⁶⁺ is required. The tetragonal phase was identified, especially because of the double peak in the 22–24° region. Three peaks would be observed in case of monoclinic or orthorhombic phases and only a single peak for the cubic phase of WO₃. In both cases the substrates peaks of TiN and Pt were identified. For Pt, this is expected since this metal is inert in the used annealing conditions. The presence of TiN is less obvious as TiN tends to oxidize to form TiO₂ while annealing in oxidative conditions.⁴⁰ Since at least part of the tungsten is reduced as-deposited, it might act as a protection to prevent (partial) oxidation of the TiN. However, CV of WO₃ on TiN (Fig. 7, left) shows small reduction and oxidation peaks at 1.6 and 2.0 V, respectively. This suggest that a fraction of TiN is oxidized during annealing at 500 °C, yielding TiO₂.⁶⁷ This leads to a possible lower conductivity of the TiN current collector. Notably, both films have a different crystal structure than the powders annealed at the same temperature. The tetragonal phase normally exists at temperatures above 700 °C (ref. 57 and 58) or by insertion of alkali ions.^{68,69} Since both are not the case, it is thought that the substrate favors the formation of the tetragonal phase at a lower annealing temperature (500 °C) and remains stable at room temperature.

Electrochemical analysis

The presence of W⁶⁺ was probed with cyclic voltammetry as was discussed above. While inserting lithium into the crystal structure, the tungsten is reduced. This is shown in eqn (5).

The CV (Fig. 7) shows that this reaction is not limited to W⁵⁺, but W⁴⁺ is also present as was previously shown. In Fig. 7, two oxidation peaks can be observed which are associated to the W⁴⁺ to W⁵⁺ and W⁵⁺ to W⁶⁺ (indicated by 3 and 4 in Fig. 7, respectively). The results are summarized in Table 2. In case of TiN a slightly larger overpotential is measured compared to Pt, especially in the case of the W⁵⁺ to W⁴⁺. This is probably due to larger resistance of the substrate, as part of the TiN is oxidized during the annealing. Significant differences are found between the type of substrates while comparing the peaks of the W⁵⁺ oxidation peak, as indicated by 4 in Fig. 7. Especially in the case of Pt the oxidation peaks have a relatively low intensity, indicating that part of the tungsten present is irreversibly reduced with Pt as a substrate.

Overall the charge/discharge measurements of WO₃ on TiN and Pt look comparable (Fig. 9), some differences will be discussed in the next paragraph. In general, for both substrates a first small voltage plateau is found at 2.7 V, which is assigned to the intercalation of Li⁺ into the tetragonal phase.^{68,69} A second, large plateau is found between 2.6 and 2.4 V, which is related to Li⁺ insertion in the cubic phase. This phase is formed

Fig. 8 XRD of 10 layers of WO₃ deposited, deposited at 150 °C. The films were submitted to a post deposition anneal of 1 hour at 500 °C in static air. Pristine WO₃ on TiN (A) and Pt (B), as compared to WO₃ after 100 cycles of charge/discharge at 1C on TiN (C) and Pt (D). References indicated as followed: TiN (▲ JCPDS 01-87-0632), Pt (▲ JCPDS 01-87-0647), Si (▲ JCPDS 01-72-1088), tetragonal WO₃ (▼ JCPDS 01-85-807) and cubic WO₃ (▼ JCPDS 20-1323).

Table 2 Peak potentials measured by cyclic voltammetry of 10 layers of WO₃ deposited on TiN and Pt, measured at 1 mV s⁻¹ in 1 M LiClO₄ in PC. The films were submitted to a post deposition anneal of 1 hour at 500 °C in static air

Substrate	Reaction	Reduction potential [V]	Oxidation potential [V]
TiN	W ⁶⁺ + e ⁻ ↔ W ⁵⁺	2.67	2.97
Pt	W ⁶⁺ + e ⁻ ↔ W ⁵⁺	2.67	2.96
TiN	W ⁵⁺ + e ⁻ ↔ W ⁴⁺	2.38	2.68
Pt	W ⁵⁺ + e ⁻ ↔ W ⁴⁺	2.40	2.68

upon sufficient lithiation ($x > 0.13$ for Li_xWO₃) of the tetragonal phase.^{68,69} Finally, a considerable amount of charge is inserted while maintaining a slight slope (*i.e.* without clearly defined voltage plateau), which suggests that amorphous phases are responsible for a considerable part of the total capacity.⁶⁹ The amorphous WO₃ is known to have a wide distribution of site energies, yielding a poorly defined voltage plateau.¹⁶ The capacity fading observed during the cause of 100 charge/discharge cycles for both WO₃/TiN and WO₃/Pt seems to be related to the destruction or irreversible lithiation of the cubic phase, as the voltage plateau between 2.6 and 2.4 V (lithiation) shortens significantly.

As was mentioned before, there are small differences while comparing the charge/discharge curves of the two substrates in Fig. 9a. First of all the capacity fading (comparing the first and hundredth cycle) is more severe for WO₃ on Pt. While referring back to the cyclic voltammetry measurements (Fig. 7), the stronger capacity fading in case of WO₃/Pt as

compared to WO₃/TiN is related to irreversible reduction of the tungsten present. In addition, the voltage plateaus of both the tetragonal and cubic phases are significantly shorter in case of Pt. This means that less tetragonal and cubic phase is available for Li insertion. Finally, the voltage slope before cut-off, previously assigned to disordered or amorphous WO₃, is significantly longer in case of Pt. All these arguments suggest a less crystalline material is available for lithiation on Pt compared to TiN.

(*Ex situ*) XRD performed on cycled films (Fig. 8, top) yield another clue what the main differences between the two substrates are. For WO₃ on TiN, a clear transition from tetragonal to cubic WO₃ can be observed upon cycling. However, in case of Pt a difference is noted. In the first place the crystallinity is significantly lower, as the peaks at 24 and 33.5° are much broader. In addition, the (100) peak at 24° is significantly shifted to the right as to compared to TiN as substrate; combined with a small peak at 34° this might imply that a mixture of cubic and predominantly tetragonal phase is present.

The poor performance of Pt as substrate is expressed as well in the charge/discharge measurements as function of cycle number (Fig. 9b). Although the overall capacity of WO₃ on TiN and Pt seems comparable at first, in case of Pt the delithiation capacity drops to a significant lower level from the 5th cycle and onward. While WO₃ on TiN leads to a steady coulombic efficiency of 99.2%, in case of Pt much more variation is observed with a maximum efficiency of 96.6%, although both samples were submitted to the same synthesis conditions and anneals. The capacity of the WO₃/TiN films surpasses the theoretical value of 0.75 Li per WO₃ unit for the cubic phase,⁶⁹ although Fig. 9b shows that after 100 cycles a more stable capacity value

Fig. 9 Charge/discharge curves of 10 layers of WO_3 deposited on TiN and annealed at 500 °C for 1 hour in static air, measured at 1C in 1.0 M LiClO_4 at 20 °C. (a) shows capacity/potential curves and (b) shows capacity and coulombic efficiency versus cycle number.

close to the theoretical maximum is reached. Very low coulombic efficiencies are registered the first cycles (starting from 82.8 and 73.1% for TiN and Pt, respectively), the capacity values surpassing theoretical values are therefore attributed to irreversible intercalation into amorphous phases as observed in the slope before cut-off noted previously (Fig. 9a). The capacity values reached are however equal to WO_3 in bulk (powder) form using a comparable voltage range,²⁰ indicating that at least in case of TiN as substrate sufficient crystallinity and phase stability is reached.

In view of device integration and oxidation of TiN into TiO_2 , lower temperature annealing temperatures were investigated by charge/discharge measurements. 300 °C appeared to be too low to yield electrochemically active material (not shown). After 1 hour at 300 °C not all the (crystal) water has left the system yet (Fig. 3), which might be an indicator for inactivity. Another explanation might be that bleaching, *i.e.* oxidation to tungsten from either W^{4+} or W^{5+} , occurs so slowly that tungsten oxide phases are insufficiently formed. It was reported previously that bleaching by thermal annealing of tungsten oxide films occurs at much lower speeds at 400 °C as compared to 500 °C in oxygen rich conditions.⁴⁸ Nevertheless, at 400 °C electrochemically active films were indeed obtained (*cf.*

Fig. S10†), although activity was significantly lower as compared to the 500 °C case for both WO_3/TiN and WO_3/Pt samples. This matches with the bleaching behavior at these temperatures.⁴⁸ However, after 100 cycles part of the Pt is visible macroscopically (not shown). This implies that due to cycling WO_3 on Pt, structural changes appear as was the case for the 500 °C anneal (Fig. 9). However, in case of the 400 °C anneal the effect seems to be more severe. Regarding adhesion in case of Pt as substrate, the film appeared to be more stable after an anneal at 500 °C as compared 400 °C. In both cases there is a drop in efficiency and capacity followed by a slight improvement between 20 and 40 cycles, it is therefore thought that the same physical process acts on the WO_3/Pt combination which is intensified at lower annealing temperatures. Adhesion of the WO_3 film to TiN is therefore regarded significantly better as compared to Pt. Nevertheless, the overall performance of WO_3/TiN at 400 °C (coulombic efficiency 99.0%, capacity of 75 mA h g^{-1} , *cf.* Fig. S10†) are lower than the same WO_3/TiN combination annealed at 500 °C (Fig. 9). These differences are ascribed to better crystallization induced by improved bleaching⁴⁸ and/or increase of oxygen vacancies²⁰ at higher annealing temperatures.

Conclusions

The chemistry of tungsten chloride in an ethanol/water mixture was explored for the synthesis of tungsten oxide films starting from a tungsten chloride-based solution. Part of the tungsten present in the precursor was reduced while forming chlorine gas and 1,1-diethoxyethane. The chlorine leaves the precursor as hydrogen chloride gas leading to a chlorine depleted precursor. In addition, *via* hydrolysis and condensation, particles were formed resulting in a colloidal suspension. *Via* ultrasonic spray deposition of the colloidal suspension and a subsequent oxidative annealing at 500 °C, electrochemically active thin films were obtained with a capacity value of 90 mA h g⁻¹ or 640 mA h cm⁻³. A clear difference in the performance was noted between the TiN and Pt substrate. The TiN allows a higher coulombic efficiency and a much more stable capacity evolution, especially in the case of an annealing temperature as low as 400 °C. The relative low annealing temperature required for the formation of active tungsten oxide thin films is an important breakthrough allowing the use of TiN as low-cost alternative for the Pt current collector. In addition, this approach opens up new possibilities for the fabrication of all-solid-state Li-ion batteries as these WO₃ films, exhibiting a high volumetric capacity, can be combined with electrochemically instable solid electrolytes such as Li_{3x}La_{(2/3)-2x}TiO₃. Arguably, the significant loss of power density expected for an all-solid-state Li-ion battery – caused by the relative high intercalation voltage the of the proposed WO₃ films – is compensated by the (i) compatibility with several (oxide-based) solid-state electrolytes, (ii) ease of processing and (iii) relative low temperature requirements. As the proposed route is a low cost method in combination with inexpensive materials, ultrasonic spray deposition of WO₃ colloidal suspensions is a promising method for upscaling purposes. This further underlines the significance of this versatile synthesis method.

Acknowledgements

The authors thank Jan Czech for performing the headspace GC-MS measurements, Giulia Maino for the helpful discussion regarding the electrochemical measurements and Prof. Jan D'Haen for discussing XRD data. Imec (Leuven, Belgium) and the CoCooN research group Ghent University (Belgium) are acknowledged for providing substrates. The Energy Materials and Devices group of Eindhoven University of Technology is acknowledged for assistance regarding the electrochemical measurements. This study was partially supported by the IWT SOS Lion project.

Notes and references

- 1 P. Knauth, *Solid State Ionics*, 2009, **180**, 911–916.
- 2 K. Takada, *Acta Mater.*, 2013, **61**, 759–770.
- 3 V. Thangadurai and W. Weppner, *Ionics*, 2006, **12**, 81–92.
- 4 J. B. Bates, N. J. Dudney, B. Neudecker, A. Ueda and C. D. Evans, *Solid State Ionics*, 2000, **135**, 33–45.
- 5 D. Pinzaru and V. Thangadurai, *J. Electrochem. Soc.*, 2014, **161**, A2060–A2067.
- 6 M. Roeder, A. B. Beleke, U. Guntow, J. Buensow, A. Guerfi, U. Posset, H. Lorrman, K. Zaghib and G. Sextl, *J. Power Sources*, 2016, **301**, 35–40.
- 7 S. Y. Tsai, K. Z. Fung and C. T. Ni, *ECS Trans.*, 2015, **68**, 37–43.
- 8 W.-J. Li and Z.-W. Fu, *Appl. Surf. Sci.*, 2010, **256**, 2447–2452.
- 9 D. G. Barton, S. L. Soled and E. Iglesia, *Top. Catal.*, 1998, **6**, 87–99.
- 10 C. Di Valentin, F. Wang and G. Pacchioni, *Top. Catal.*, 2013, **56**, 1404–1419.
- 11 J. P. Perereira-Ramos, R. Baddour-Hadjean, N. Kumagai and K. Tanno, *Electrochim. Acta*, 1993, **38**, 431–436.
- 12 K. Huang and Q. Zhang, *Nano Energy*, 2012, **1**, 172–175.
- 13 A. Yu, N. Kumagai, Z. Liu and J. Y. Lee, *J. Solid State Electrochem.*, 1998, **2**, 394–400.
- 14 G. A. Niklasson and C. G. Granqvist, *J. Mater. Chem.*, 2007, **17**, 127–156.
- 15 M. Regragui, M. Addou, A. Outzourhit, J. C. Bernede, E. El Idrissi, E. Benseddik and A. Kachouane, *Thin Solid Films*, 2000, **358**, 40–45.
- 16 J. Garcianadas, *Solid State Ionics*, 2004, **175**, 521–525.
- 17 K. Nishio, T. Sei and T. Tsuchiya, *J. Ceram. Soc. Jpn.*, 1999, **107**, 199–203.
- 18 C. Guo, S. Yin, M. Yan, M. Kobayashi, M. Kakihana and T. Sato, *Inorg. Chem.*, 2012, **51**, 4763–4771.
- 19 J. Denayer, P. Aubry, G. Bister, G. Spronck, P. Colson, B. Vertruyen, V. Lardot, F. Cambier, C. Henrist and R. Cloots, *Sol. Energy Mater. Sol. Cells*, 2014, **130**, 623–628.
- 20 W. Li, A. Sasaki, H. Oozu, K. Aoki, K. Kakushima, Y. Kataoka, A. Nishiyama, N. Sugii, H. Wakabayashi, K. Tsutsui, K. Natori and H. Iwai, *Microelectron. Reliab.*, 2015, **55**, 402–406.
- 21 P. V Braun, J. Cho, J. H. Pikul, W. P. King and H. Zhang, *Curr. Opin. Solid State Mater. Sci.*, 2012, **16**, 186–198.
- 22 J. F. M. Oudenhoven, L. Baggetto and P. H. L. Notten, *Adv. Energy Mater.*, 2011, **1**, 10–33.
- 23 P. H. L. Notten, F. Roozeboom, R. A. H. Niessen and L. Baggetto, *Adv. Mater.*, 2007, **19**, 4564–4567.
- 24 J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr and A. Choudhury, *J. Power Sources*, 1993, **44**, 103–110.
- 25 H. I. Schlesinger, H. C. Brown, A. E. Finholt, X. Y. J. B. Bates, G. E. Jellison and F. X. Hart, *J. Electrochem. Soc.*, 1997, **144**, 524–532.
- 26 J. Kawamura, *Solid State Ionics*, 2004, **175**, 273–276.
- 27 Y.-C. Perng, J. Cho, S. Y. Sun, D. Membreno, N. Cirigliano, B. Dunn and J. P. Chang, *J. Mater. Chem. A*, 2014, **2**, 9566.
- 28 S. Kim, M. Hirayama, S. Taminato and R. Kanno, *Dalton Trans.*, 2013, **42**, 13112–13117.
- 29 J. Reinacher, S. Berendts and J. Janek, *Solid State Ionics*, 2014, **258**, 1–7.
- 30 K. Tadanaga, H. Egawa, A. Hayashi, M. Tatsumisago, J. Mosa, M. Aparicio and A. Duran, *J. Power Sources*, 2015, **273**, 844–847.
- 31 S. Stramare, V. Thangadurai and W. Weppner, *Chem. Mater.*, 2003, **15**, 3974–3990.

- 32 Y. J. Shan, L. Chen, Y. Inaguma, M. Itoh and T. Nakamura, *J. Power Sources*, 1995, **54**, 397–402.
- 33 Y. Inaguma, C. Lique, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta and M. Wakihara, *Solid State Commun.*, 1993, **86**, 689–693.
- 34 E. J. van den Ham, N. Peys, C. De Dobbelaere, J. D'Haen, F. Mattelaer, C. Detavernier, P. H. L. Notten, A. Hardy and M. K. Van Bael, *J. Sol-Gel Sci. Technol.*, 2015, **73**, 536–543.
- 35 S. Furusawa, H. Tabuchi, T. Sugiyama, S. Tao and J. Irvine, *Solid State Ionics*, 2005, **176**, 553–558.
- 36 K. Kiaoka, H. Kozuka, T. Hashimoto and T. Yoko, *J. Mater. Sci.*, 1997, **32**, 2063–2070.
- 37 C. Delmas, A. Nadiri and J. L. Soubeyroux, *Solid State Ionics*, 1988, **28–30**, 419–423.
- 38 K. Takada, M. Tansho, I. Yanase, T. Inada, A. Kajiyama, M. Kouguchi, S. Kondo and M. Watanabe, *Solid State Ionics*, 2001, **139**, 241–247.
- 39 L. Baggetto, J. F. M. Oudenhoven, T. Van Dongen, J. H. Klootwijk, M. Mulder, R. A. H. Niessen, M. De Croon and P. H. L. Notten, *J. Power Sources*, 2009, **189**, 402–410.
- 40 N. C. Saha and H. G. Tompkins, *J. Appl. Phys.*, 1992, **72**, 3072.
- 41 K. Nishio and T. Tsuchiya, *Sol. Energy Mater. Sol. Cells*, 2001, **68**, 279–293.
- 42 L. Muresan, E. J. Popovici, A. R. Tomsa and E. Indrea, *J. Optoelectron. Adv. Mater.*, 2008, **10**, 2261–2264.
- 43 D. B. Kokh, A. B. Alekseyev and R. J. Buenker, *J. Chem. Phys.*, 2004, **120**, 11549–11556.
- 44 O. J. Klejnot, *Inorg. Chem.*, 1965, **4**, 1668–1670.
- 45 K. Arbi, S. Mandal, J. M. Rojo and J. Sanz, *Chem. Mater.*, 2002, **14**, 1091–1097.
- 46 M. I. Bernal-Uruchurtu, G. Kerenskaya and K. C. Janda, *Int. Rev. Phys. Chem.*, 2009, **28**, 223–265.
- 47 S.-H. Wang, T.-C. Chou and C.-C. Liu, *Sens. Actuators, B*, 2003, **94**, 343–351.
- 48 G. Leftheriotis, S. Papaefthimiou, P. Yianoulis and A. Siokou, *Thin Solid Films*, 2001, **384**, 298–306.
- 49 L. Berggren, J. C. Jonsson and G. a. Niklasson, *J. Appl. Phys.*, 2007, **102**, 083538.
- 50 D. Dini and F. Decker, *J. Appl. Electrochem.*, 1996, **26**, 647–653.
- 51 S. Darmawi, S. Burkhardt, T. Leichtweiss, D. a. Weber, S. Wenzel, J. Janek, M. T. Elm and P. J. Klar, *Phys. Chem. Chem. Phys.*, 2015, **17**, 15903–15911.
- 52 X. He and H. Liu, *Catal. Today*, 2014, **233**, 133–139.
- 53 M. Kaufhold and M. El-Chahawi, *US Pat.*, 5,527,969, Huels Aktiengesellschaft, 1996.
- 54 M. R. Capeletti, L. Balzano, G. de la Puente, M. Laborde and U. Sedran, *Appl. Catal., A*, 2000, **198**, L1–L4.
- 55 J. Livage and D. Ganguli, *Sol. Energy Mater. Sol. Cells*, 2001, **68**, 365–381.
- 56 H. Ryu, K. Park, I. Kim, K. Hong, W. Lee and J. Park, *Synthesis and characterization of WO₃ nanopowders and their electrical properties*, 2003, vol. 42, pp. 727–730.
- 57 T. Vogt, P. M. Woodward and B. A. Hunter, *J. Solid State Chem.*, 1999, **144**, 209–215.
- 58 S. Pokhrel, J. Birkenstock, A. Dianat, J. Zimmermann, M. Schowalter, A. Rosenauer, L. C. Ciacchi and L. Mädler, *CrystEngComm*, 2015, **17**, 6985–6998.
- 59 R. W. Schwartz, T. Schneller and R. Waser, *C. R. Chim.*, 2004, **7**, 433–461.
- 60 D. Perednis and L. J. Gauckler, *J. Electroceram.*, 2005, **14**, 103–111.
- 61 M. Majumder, C. Rendall, M. Li, N. Behabtu, J. A. Eukel, R. H. Hauge, H. K. Schmidt and M. Pasquali, *Chem. Eng. Sci.*, 2010, **65**, 2000–2008.
- 62 A. Temmink, O. Anderson and K. Bange, *Thin Solid Films*, 1990, **192**, 211–218.
- 63 G. Hollinger and T. M. Duc, *Phys. Rev. Lett.*, 1976, **37**, 1564–1567.
- 64 C. Cantalini, H. T. Sum, M. Faccio, M. Pelino, S. Santucci, L. Lozzi and M. Passacantando, *Sens. Actuators, B*, 1996, **31**, 81–87.
- 65 T. J. Driscoll, L. D. McCormick and W. C. Lederer, *Surf. Sci.*, 1987, **187**, 539–558.
- 66 P. L. Hagedoorn, J. R. Freije and W. R. Hagen, *FEBS Lett.*, 1999, **462**, 66–70.
- 67 Z. He, Z. Wang, F. Wu, H. Guo, X. Li and X. Xiong, *J. Alloys Compd.*, 2012, **540**, 39–45.
- 68 Q. Zhong, J. R. Dahn and K. Colbow, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 2554–2560.
- 69 K. H. Cheng and M. S. Whittingham, *Solid State Ionics*, 1980, **1**, 151–161.