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Comparison Between CVD and ALE Produced TiO₂ Cathodes in Zn/(PEO)₄ZnCl₂/TiO₂,SnO₂ or ITO Galvanic Cells

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Abstract. The way of preparation of thin films of TiO₂ is extremely important regarding its application in electronic and optoelectronic devices. We have assembled Zn/(PEO)₄ZnCl₂/TiO₂,SnO₂ or ITO rechargeable galvanic cells using CVD (chemical vapour deposition) or ALE (atomic layer epitaxy) produced TiO₂ cathodes. The charge-discharge cycles were measured with a constant current in the range of 10⁻⁶ to 10⁻⁵ A for different cells. It was shown that CVD prepared TiO₂ cathode is increasing capacity of the cell by allowing higher constant currents to be applied to the cell. The complex impedance measurements of the electrolyte (PEO)₄ZnCl₂ have been performed in the range of 1 Hz to 1 MHz and in the temperature range from 290 to 400 K by applying Zn or Sn electrodes.

1. INTRODUCTION

Titanium dioxide films were employed as intercalation electrodes with solid polymeric electrolyte in order to achieve a stable and low cost solid-state galvanic cell, which has good stability in adverse environments. TiO₂ and polymer salt complex of poly(ethylene oxide) (PEO)₄ and ZnCl₂ were chosen because of possibility for simple and cheap preparation methods.

Two preparation methods were employed in order to obtain TiO₂ thin films: CVD (chemical vapour deposition) and ALE (atomic layer epitaxy). We have studied electrical properties of thin films Zn/(PEO)₄ZnCl₂/TiO₂,SnO₂ or ITO rechargeable galvanic cells using CVD or ALE prepared TiO₂ in different cells. The capacities of the so assembled cells varied depending on the type of preparation of TiO₂ cathodes.

2. EXPERIMENTAL DETAILS

Thin films galvanic cells were prepared according to the schemes: Zn/(PEO)₄ZnCl₂/TiO₂ (CVD), SnO₂ and Zn/(PEO)₄ZnCl₂/TiO₂ (ALE), ITO.

The chemical vapour deposition and atomic layer epitaxy were used to obtain TiO₂ samples of different morphologies, which are both transparent but differ in grain sizes, smoothness and electrical resistivities.

The polymer salt complex was prepared by dissolving ZnCl₂ and poly(ethylene-oxide) (MW= 4 × 10⁶) in 50% ethanol-water solution in stoichiometric proportions. The polymer-complex salt solution was then poured on teflon plate and allowed to dry in air. The film was evacuated for a few

days to allow for traces of solvent to evaporate.

In the CVD method [1-5] we have used a commercial (Merck) TiCl_4 . A schematic diagram of the apparatus used is shown Fig. 1. Air used as a carrier gas flow through pipe (1) at a rate of 10 ml/min. The sublimated vapour of TiCl_4 is carried away through pipe (2) to a clean substrate (glass, quartz) placed on a plate heated at 370°C . At the heated substrate TiCl_4 molecules receive enough energy to interact with moisture from air:

Fig. 1. The layout of the apparatus for CVD of TiO_2 thin films in normal atmosphere

The growth rate of the films was typically 5 nm/s. The thickness of the film was approximately 300 nm.

The second way of obtaining TiO_2 thin films was atomic layer epitaxy (ALE) [6-9]. ALE offers a possibility to deposit ITO and TiO_2 films in a one continuous process which is apparently beneficial in respect to the control of the interface between these two films. The ALE deposition of TiO_2 and ITO films was carried out with a commercial flow type F 120 reactor (Microchemistry Ltd., Espoo, Finland) operated under pressure of 10 mbar. Nitrogen served both as a carrier and purging gas. The films were deposited onto $5 \times 5 \text{ cm}^2$ soda lime glass substrate at 500°C . TiCl_4 , InCl_3 , SnCl_4 and water were employed as reactants. A detailed description of the TiO_2 and In_2O_3 deposition has been given in Refs. 6 and 7, respectively. For the doping of In_2O_3 , SnCl_4 was vaporised in an external reservoir tempered at 10°C and led into reactor as described for TiCl_4 [6]. The doping was accomplished using a pulsing sequence of $(\text{In-O})_{96}(\text{Sn-O})_4(\text{In-O})_{96}$... found to give the lowest resistivity of the order of $2 \times 10^{-4} \Omega\text{cm}$ [8]. The thicknesses of both the TiO_2 and ITO films were about 100 nm.

The CVD method for preparation of SnO_2 thin films was modified [10] by using solid components, namely tin iodide, SnI_4 , and antimony iodide, SbI_3 , and the effect of sublimation.

Impedance measurements were performed with the meter which was built in our laboratory. It has frequency range from 0.1 Hz to 3 MHz. Charge-discharge cycles of the galvanic cells were automatically recorded with the laboratory maintained set-up of Keithley voltmeters, ampermeters, current source and laboratory made switch device, all on-line to PC.

The crystal structure and crystal orientation were determined by X-ray diffraction (XRD) measurements with a Phillips powder diffractometer MPD 1880 and Debye-Scherrer camera using $\text{CuK}\alpha$ radiation. Surface morphology was characterised by a JEOL JSEM - 820 scanning electron microscope. The thickness and refractive indices of films were evaluated by fitting measured transmittance curves according to the matrix method used commonly for calculation of thin film optical device performance [6]. Also, the film thickness was determined with a Tencor alpha-step instrument.

3. RESULTS AND DISCUSSION

3.1 Microstructural properties of TiO_2 films

The resistivities of CVD obtained TiO_2 samples were lower ($\rho = 2.2 \times 10^3 \Omega\text{cm}$) than by ALE prepared smooth films ($\rho = 4 \times 10^5 \Omega\text{cm}$), which consisted of grains with diameter of about $0.1 \mu\text{m}$ (SEM) [6]. As examined with XRD, the TiO_2 film grown by ALE exhibited only rather weak reflections of both the anatase and rutile phases.

X-ray diffraction and Raman spectroscopy have shown for CVD obtained samples to be in the anatase form and that crystallite sizes were $50.1 \pm 0.2 \text{ nm}$ [1].

3.2. Impedance spectroscopy

The complex impedance of polyelectrolyte was measured between 10 Hz and 500 kHz. The samples (film disks with radius $\approx 1 \text{ cm}$ and $\approx 0.2 \text{ mm}$ thickness) mounted between two zinc or Sn electrodes were placed in spring-contacted apparatus compressing the cell between teflon with Zn cylinders. Measurements were consistent with model circuits [11] representing the sample/electrode system as parallel sample resistance and capacitance in series with two impedances representing the electrode and electrolyte characteristics.

Fig. 2. $\log \sigma$ versus $1000/T$ for measurements II

3.2.1. Temperature dependence of conductivity of polyelectrolyte $(\text{PEO})_4\text{ZnCl}_2$

3.2.1.1 Blocking electrodes (Sn): With blocking electrodes (Sn) measurements were performed in impedance representation and in two different regimes. In the first experiment (I) heating was discontinuous as measurements have been performed during few days. The sample was cooled to the room temperature and stayed at it during the nights. Second type of measurements (II) were performed with continuous heating in non-interrupted temperature range from room temperature to 135°C . Based on the shape of curves we could represent impedances with one or two parallel equivalent circuits. At low temperatures we have parallel R_b (bulk) resistance and C_g (geometrical)

capacitance in series with C_{dl} (double layer) capacitance. High temperature measurements showed R_{ct} (charge transfer) resistance parallel to C_{dl} in series with other parallel circuit: R_b and C_g .

The results of the measurements between room temperature and 135 °C are presented in Fig. 2.

A non-linear type of behaviour can be observed on this plot. To interpret the variation of the conductivity as a function of temperature we made use of a transport theory based on the free-volume Vogel-Tamman-Fulcher equation [12]:

$$\sigma = AT^{-1/2} \exp[-E_a/K(T - T_0)] \quad (2)$$

In this model, suitable for concentrated solutions, fused salts and amorphous poly(ethylen-oxide) alkali metal complex salts [13,14], the diffusion of ions depends on disordered local movements in the material. In this equation, T_0 represents the ideal vitreous transition temperature. A is proportional to the concentration of charge carriers and to the geometric factor and E_a is a pseudo-activation energy. With this model the data can be easily linearized, by plotting $[\ln(\sigma\sqrt{T}/A)]^{-1}$ versus T , having access to the parameters E_a , T_0 and A as shown in Fig. 3.

Fig. 3. Plot of $[\ln(\sigma\sqrt{T}/A)]^{-1}$ vs. T for $(\text{PEO})_4\text{ZnCl}_2$

3.2.1.2 Non-blocking electrodes (Zn): For non-blocking Zn electrodes measurements were performed in impedance and admittance modes, because R_b had to be determined at very high frequencies and in impedance mode it was at the limit of the range for the instrument. Measuring admittance at lower temperatures below 100°C we have obtained one arc, while above 100°C one more arc has appeared. At low temperatures C_{dl} vanishes because at non-blocking electrodes there is a significant charge transfer between electrolyte and electrodes.

At high temperatures we have observed another arc at low frequencies, which is attributed to capacity between grain boundaries. By "grains" we have assumed amorphous conducting areas in electrolyte divided by spherulites. As R_{gb} (grain boundaries) is much bigger than R_b , and could be determined at high frequencies, we can assume only C_{gb} in impedance circuit.

Activation energy obtained in this measurements with Zn electrodes is lower than with blocking ones. This can be explained with intensive transport of ions between electrodes and electrolyte which increases a number of conducting ions in electrolyte and enhances process of ionic conduction.

The constants: A , pseudo-activation energies E_a and ideal vitreous transition temperature T_0 are given in Table 1.

Table 1. A , pseudo-activation energies E_a and ideal vitreous transition temperatures T_0 .

ELECTRODE	$\log A$	E_a (eV)	T_0 (K)
Sn(I)	-1.12	0.12	205
Sn(II)	-1.58	0.049	247
Zn	-4.38	0.0073	229

Higher activation energy for Sn(I) is connected with thermal history of sample, which was heated discontinuously. Multiple heating and cooling have increased a quantity crystalline part of the sample which is a non-conductive area. This situation is compatible with higher activation energy E_a .

3.2.2. Conductivity as a function of exposure to air

These measurements have been performed in order to evaluate behaviour of a sample in room temperature atmospheric conditions, where we have focused on its previously known hygroscopy [15,16]. Measurements of impedance or admittance curves were done on previously evacuated sample with time intervals of 15 min. All the time the sample was at 20°C and humidity of air was 65%.

Fig. 4. Charge-discharge curves for the battery $\text{Zn}/(\text{PEO})_4\text{ZnCl}_2/\text{TiO}_2$ (CVD), SnO_2 (1) at a constant current of $I = 10 \mu\text{A}$.

Two types of measurements were done: one with sample which was exposed to multiple heating and cooling cycles, and one with "fresh" sample. Results of measurements show that there is difference between two cases: 1) at the previously cycled sample we had linear increase of conductivity and at the end it became like a glue; 2) "fresh" sample had almost constant conductivity value for almost three hours of measurements and no physical changes could be seen.

These measurements are relevant for the application of polyelectrolyte in galvanic cell.

3.3. Potential-time characteristic of galvanic cells

The cell $\text{Zn}/(\text{PEO})_4\text{ZnCl}_2/\text{TiO}_2$ (CVD), SnO_2 was charged with constant current $I = 10 \mu\text{A}$ (Fig. 4). It has been possible to recharge this cell up to 50 cycles with a constant current from $5 \mu\text{A}$ to $40 \mu\text{A}$. Charging was performed until the plateau was achieved and voltage did not change considerably (approximately 0.01 V) for about 30 min, the discharging was stopped when the voltage dropped to 1 V . Number of cycles differed from foil to foil of polyelectrolyte ranging from 35 to 50 cycles giving total capacity (as sums of capacities in all cycles) of 0.2 mAh to 0.6 mAh and maximal voltage achieved was $V_{\text{max}} = 3.5 \text{ V}$. Fig. 4 shows 34th–38th of total 38 cycles in the third round of total cycling process.

The cell $\text{Zn}/(\text{PEO})_4\text{ZnCl}_2/\text{TiO}_2(\text{ALE})$, ITO was charged with constant current of $I = 1 \mu\text{A}$ (Fig. 5). It has been possible to recharge this cell up to 1100 cycles with a constant current of $1 \mu\text{A}$. Charging cycles for this cell lasted each for about 1 min. Total capacity of the cell as sum of

Fig. 5. Charge-discharge curves for the battery $\text{Zn}/(\text{PEO})_4\text{ZnCl}_2/\text{TiO}_2(\text{ALE})$, ITO at a constant current of $I = 1 \mu\text{A}$.

capacities in all cycles was 0.17 mAh and maximal voltage was $V_{\text{max}} = 2.75 \text{ V}$ from 500 to 1100 cycle. In the first part (from 0 to 500 cycles) it had varied from 7 V to 4 V .

Comparison between overall capacities, currents and voltages for these two galvanic cells are shown in Table 2.

Table 2. Capacities, constant currents, maximal voltages and times of duration of batteries (1) and (2).

Type of cell	C (mAh)	I_{av} (μA)	V_{max} (V)	T_h (h)
(1)	0.2-0.6	5-40	3.5	35
(2)	0.17	1	2.75	168

The cell (1) with TiO_2 (CVD) shows higher capacity than the cell with TiO_2 prepared by ALE. On the other hand, overall life of cell (2) is longer than cell (1).

4. CONCLUSION

By means of electrical measurements we have shown that polyelectrolyte of polymeric complex with metal salt (ZnCl_2) can be combined among other metal oxides, with TiO_2 as intercalation cathode in order to obtain rechargeable all solid state cells. The methods of preparation (CVD, ALE) of TiO_2 resulting in different morphologies of the films influence the performance of the galvanic cells. More dense structure of ALE grown TiO_2 films as compared to CVD obtained films hinders its Zn^{2+} ions storage property. Used as an intercalation cathode TiO_2 (ALE) film was thus responsible for the lower capacity and lower charging current for this galvanic cell. On the other hand, the same property was probably responsible for its better stability and longer cycling life.

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