

ALD-processed protective layers for the MCFC state of the art cathode

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ABSTRACT

In the world of alternative energy sources, Molten Carbonate Fuel Cells (MCFC) are one promising technology for the efficient use of hydrogen to produce energy, these fuel cells work based in the carbonate cycle to get energy in form of electricity from the electrochemical process taking place at the stacks. This fuel cells work at temperatures above 600° C with molten eutectic mixtures of Li-K or Li-Na carbonates under atmospheres of CO₂/O₂ at the cathode and H₂O/H/CO₂ at Anode. One of the main issues for optimizing the MCFC is the control of the corrosion and dissolution of the state of the art porous nickel oxide cathode. A protective coating constituted by more stable oxides seems to be the best solution. In this paper, very thin layers of TiO₂ (50 and 300 nm) were processed by a sequential CVD technique known as Atomic Layer Deposition (ALD), which produces high quality, homogeneous and conformal layers. Structural, morphological and electrochemical behaviors of TiO₂-coated samples were tested in a Li₂CO₃-K₂CO₃ (62-38 mol %) eutectic melt under a standard cathode atmosphere (CO₂/air 30:70%). Ni solubility was determined by ICP-AES. The protective role of TiO₂ layers and the consequent decrease in Ni solubility have been clearly evidenced.

1. Introduction

Fuel cells are a promising technology for alternative energy generation, many types exist and their working principles determine their suitability for different applications ranging from micro-scale portable low temperature fuel cells like Polymer Exchange Membrane (PEM) to stationary megawatt scale high temperature fuel cells like Molten Carbonate FC (MCFC). These cells are suitable for stationary energy generation due to their resistance to poisoning, internal reforming ability and the less expensive construction compared to other fuel cells that incorporate precious metals like platinum into their materials. Even do MCFC technology has been around for decades, there are still many challenges in what material science and stack engineering concerns. One of the main issues of the molten

carbonate fuel cells (MCFC) operating at temperatures around 650°C, is the short lifetime of the cell components due to material degradation. Furthermore, the components of the fuel cell such as the anode, cathode, electrolyte matrix, current collectors and interconnectors which are exposed to corrosive environments are required to last up to 40,000 hours of operation for being feasible for commercial purposes [1].

The state-of-the-art MCFC cathode is constituted by porous Ni which is oxidized and lithiated *in situ* to form $\text{Li}_x\text{Ni}_{1-x}\text{O}$. This oxide tends to dissolve partially into the carbonate melt. Ni^{2+} diffuses to the anode where it can be reduced by hydrogen yielding metallic nickel, which causes a short circuit between the anode and cathode resulting in a MCFC stack failure [2,3]. In the last decade several approaches have been proposed to protect the MCFC's cathode [4-6]; however, it is still delicate to fully overcome the feasibility for commercial production. Thus, in order to increase long-term protection, titania coatings were prepared using atomic layer chemical vapor deposition (ALCVD), known as atomic layer deposition (ALD). ALD is a chemical gas phase deposition technique developed in Finland in the 1970's by T. Suntola [7].

In ALD, reactant gas pulses are separately introduced to the substrates to be coated. Growth is achieved through self-terminating surface reactions. Self-terminating means that only one monolayer of reactant gas species can be adsorbed to the surface during a pulse. The pulses containing reactant gases are separated by purging pulses where the ALD reactor is flushed with an inert gas. The purging pulses ensure that the reactant gas pulses do not mix. Mixing of the reactant gas pulses would lead to continuous growth and the accurate thickness control of the deposition process would be lost. By-products like detached ligands and excess reactants are also flushed away by the purging pulses. A complete set of reactant gas pulses and purging pulses needed to deposit a certain compound are referred to as a cycle. If deposition parameters have been chosen properly, the number of cycles rather than the concentration of the reactant species determines the film thickness [8]. Therefore, the aim of this investigation was to test deposition of different metal oxides and evaluate the performance of ALD-processed TiO_2 on porous Nickel substrate as protective layer for MCFC cathode application by determining the electrochemical behavior, surface changes and nickel solubility in an electrolyte eutectic mixture of Li_2CO_3 - K_2CO_3 (62-38 mol %) under standard cathode atmosphere.

2. Experimental

2.1 Layer deposition using ALD

A known deposition route was followed using halide-free and non-corrosive precursors, thin layers of TiO_2 , Nb_2O_5 , CeO_2 or Co_3O_4 were deposited on a commercial Si(1 1 1) substrate, and TiO_2 was deposited also on porous nickel substrate (produced by Doosan, South-Korea) by means of ALD technique using a vertical flow type reactor (Picosun SUNALE™ R-series). Titanium isopropoxide, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, Niobium Ethoxide $\text{Nb}(\text{OCH}_2\text{CH}_3)_5$,

Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)Cerium(IV) Ce(TMHD)_4 and Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) Cobalt(III) Co(TMHD)_3 were used as precursors and distilled water or O_3 as oxidizing agent. In order to prepare the layer [9-12]. Precursor and oxidant on each case were introduced into the reactor chamber using the parameters in TABLE 1.

Table 1. Deposition parameters of different metal oxides used.

Deposited Material	Precursor	Precursor temperature (°C)	Precursor pulse time (s)	Precursor purge time (s)	Oxidizing agent	Oxidant pulse time (s)	Oxidant purge time (s)	Chamber temperature (°C)
TiO_2	$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$	60	0.5	2	H_2O	0.5	2	250
Nb_2O_5	$\text{Nb}(\text{OCH}_2\text{CH}_3)_5$	110	0.2	2	H_2O	2	0.5	300
CeO_2	Ce(TMHD)_4	180	3	2.5	O_3	4	2.5	300
C_3O_4	Co(TMHD)_3	160	1.5	3	O_3	1.5	6	240

2.2 Electrochemical cell

Lithium and Potassium carbonates, of high grade purity >98% (Sigma-Aldrich®), were mixed in a proportion of 68-32mol%. The high-temperature electrochemical cell was a single-compartment alumina Al_2O_3 . Temperature was kept at a constant temperature of 650°C by means of a calibrated chromel/alumel thermocouple. The standard cathode atmosphere was a mixture of Air/ CO_2 (70/30 mol%) of high grade purity (Liquid Air®) at 650°C and a pressure of 1 atmosphere. For each TiO_2 -coated sample, a carbonate melt was prepared and stabilized 24 h at 650°. After stabilizing the molten carbonate eutectic under the selected cathode atmosphere, samples were immersed in the melt and electrochemical measurements were performed for 230 h. After electrochemical tests, the samples were rinsed with deionized water to remove the carbonates, dried at 100°C in an oven and kept in small plastic boxes to prevent contamination before further analysis. The samples were then renamed as TiO_2 -1A and TiO_2 -2A.

2.3 Physical, Chemical and Electrochemical Characterization

TiO_2 on Ni porous samples were characterized before and after the electrochemical test by XRD and SEM-EDS, electrochemical tests consisted on Electrochemical Impedance Spectroscopy (EIS). XPS was employed for the tested samples after immersion in molten carbonate eutectics to determine the Ni, Ti and Li species in each sample.

3. Results and Discussion

Figure 1a) shows layers of different oxides made by ALD technique; the layer is dense, homogenous in some cases and covers all the Si (111) substrates. Figure 1b) corresponds to TiO_2 films of 50 and 300 nm deposited on Ni porous substrate; a layer is present in all the surface and cavities as an homogenous, dense layer.

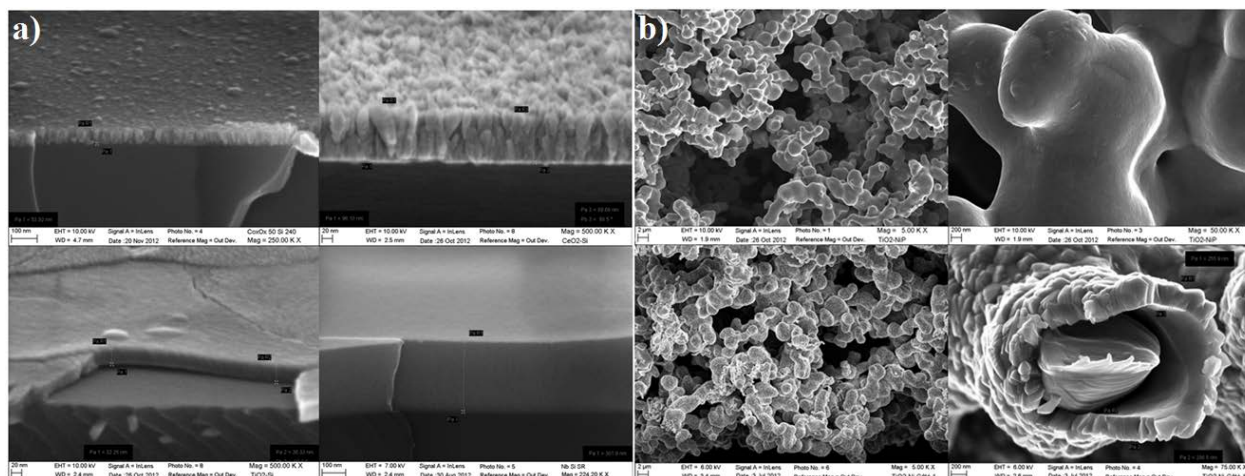


Figure 1. a) Different materials deposited by ALD on Si (1 1 1): up left Co_3O_4 , up right CeO_2 , bottom left TiO_2 and bottom right Nb_2O_5 . b) TiO_2 layers deposited in Ni porous substrates: up row 50 nm, bottom row 300 nm.

Titanium oxide layers were tested electrochemically, the EIS data was fitted from Nyquist pots using an equivalent circuit composed by one resistance (R_e) in series with two arrays each conformed by a resistance (R_c , R_p) and a CPE both arrays are in series. The data obtained from the analysis was the evolution of resistances R_e , R_c and R_p as a function of time shown in Figure 2. Analyzing the impedance diagrams, the TiO_2 -coated Ni largely decreases the total resistance of the system. Moreover, the thicker is the coating the lower is the resistance: at 10-2 Hz for instance, $R(\text{TiO}_2 - 1\text{A}) = 0.7 \, \Omega$ and $R(\text{TiO}_2 - 2\text{A}) = 1.2 \, \Omega$, which is almost 6 times lower than the system resistance based on uncovered porous Ni. A focus on the highest frequencies used in these diagrams allowed us measuring the electrolyte resistance. Its variations are reported in Figure 2 as a function of immersion time, for the three samples used as working electrodes. These electrolyte values evolve during the immersion duration. Three main zones can be distinguished for porous nickel as well as for TiO_2 -1A, and mainly 2 for TiO_2 -2A. The different values of electrolyte resistance, obtained in strictly the same conditions, are surely caused by the variation of the working electrode surface value. The initial geometrical surface is the same whatever the sample considered. Nevertheless, two of them are TiO_2 -coated. Thus, the specific surface area, and as a direct consequence the electrochemically active surface area are modified from a sample to another. Electrolyte resistance decrease is a result of an increase in the surface, which means that the 300 nm deposit presents a largely higher specific surface area than the others. After 180 hours of immersion, the electrolyte resistance is lower when using TiO_2 -1A 50, which could indicate a less effective modification of the phase and the film, and thus of the surface area

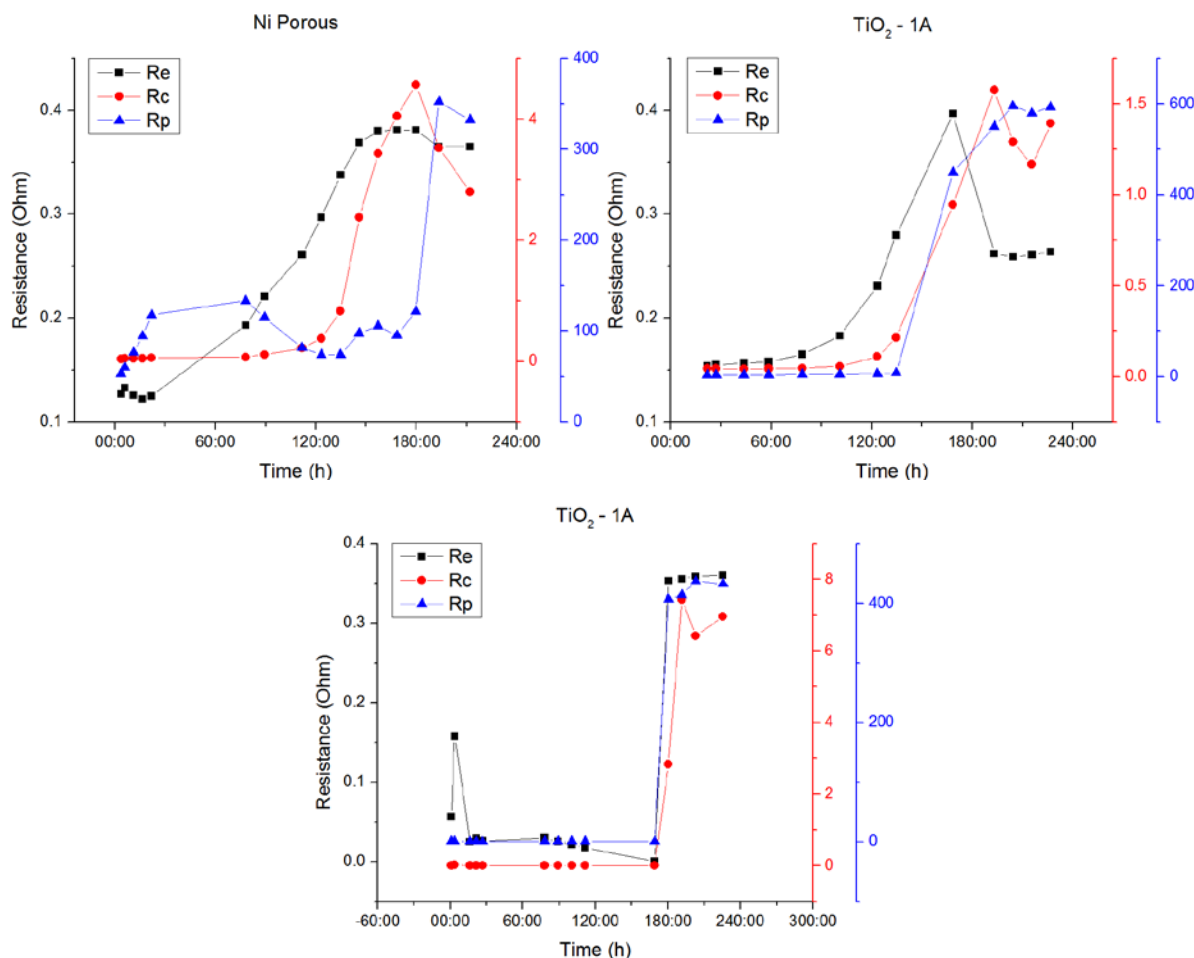


Figure 2. Resistances of Ni Porous, TiO₂-1A (50 nm) and TiO₂-2A (300 nm) measured by equivalent circuit fitting.

4. Conclusions

This paper not only confirms the promising features of titanium-based materials for optimizing the operation of MCFC devices, which has been previously developed in a few papers, but also gives a good scientific background for the integration of TiO₂ as an ultrathin coating for the protection of the state of the art cathode. The use of a high-quality technique such as ALD, which scalability is already proven in electronic or electroluminescence industries, allowed processing TiO₂-coatings, crystalline as deposited at 250°C without any further annealing process. It can be deduced that the TiO₂-coating is favorable to the whole reduction process but the tendency is reversed after 150 h of immersion. Longer immersion times would be necessary to analyze more precisely the evolution of the coated samples. In any case, all these results show the feasibility of such high-quality coatings enriched progressively by

nickel diffusion to form a stable compound, which protects the porous nickel substrate and decreases significantly nickel solubility. Furthermore, titanium solubility is extremely low in molten carbonates and this is a key aspect to integrate it in MCFC devices.

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