Electrochimica Acta 140 (2014) 174–181

Contents lists available at ScienceDirect

Electrochimica Acta

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

Electrochemical properties of Atomic layer deposition processed CeO_2 as a protective layer for the molten carbonate fuel cell cathode

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ARTICLE INFO

Article history:
Received 15 December 2013
Received in revised form 5 May 2014
Accepted 5 May 2014
Available online 14 May 2014

Keywords:
MCFC
Cathode
Cerium oxide
Coating
ALD
Electrochemistry

ABSTRACT

In order to increase the lifetime and performance of the molten carbonate fuel cell, it is compulsory to control the corrosion and dissolution of the state of the art porous nickel oxide cathode. A protective coating constituted by more stable oxides appears to be the best approach. Previous research on CeO_2 coatings obtained by DC reactive magnetron sputtering to protect the Molten carbonate fuel cell cathode gave promising results but it was necessary to improve the coating adhesion. In this paper Atomic Layer Deposition, producing high quality, homogeneous and conformal layers, was used to obtain thin layers of CeO_2 (20 nm and 120 nm) deposited over porous nickel. CeO_2-Ni coated samples were tested as cathodes in Li_2CO_3-K_2CO_3 (62-38 mol %) eutectic mixture under standard cathode atmosphere (CO_2/air 30:70 vol. %). Structural and morphological characterizations of the nickel coated cathode before and after electrochemical tests in the molten carbonate melt are reported together with the Open Circuit Potential evolution all over 230 h for both the bare porous nickel and the CeO_2-coated samples.

1. Introduction

Fuel cells (FC) are a promising technology for alternative energy generation. Different 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 (PEMFC) to stationary megawatt scale high temperature fuel cells like Solid Oxide (SOFC) and Molten Carbonate (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. Even though MCFC technology has been around for decades, there are still many challenges regarding material science and stack engineering breakthroughs. One of the main issues of the MCFC operating at temperatures around 650 °C, is the short lifetime of the cell components due to material degradation. Furthermore, MCFC components such as the anode, cathode, electrolyte matrix, current collectors and interconnectors which are exposed to corrosive environments are required to last more than 40,000 hours of operation for being feasible at a commercial level [1].

The state of the art MCFC cathode is constituted by porous Ni which is oxidized and lithiated *in situ* to form $Li_xNi_{1-x}O$. 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 cathode [4–10]; however, it is still delicate to establish their feasibility for commercial production.

Ceria has been previously studied in the literature under MCFC conditions demonstrating that it is a promising oxide to reduce Ni dissolution due to its stability [7,9,10]. Thus, in order to increase long-term protection of the Ni cathode, ceria coatings were processed in the present work by Atomic Layer Chemical Vapor deposition (ALCVD), also known as atomic layer deposition (ALD) similar to a sequential CVD. ALD is a chemical gas phase deposition technique developed in Finland in the 1970s by T. Suntola [11]. Even though this technique is relatively expensive it offers several advantages: high-quality ultrathin films, homogenous, conformal, crystalline as-deposited and scalability, *e.g.* large-area flat

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http://dx.doi.org/10.1016/j.electacta.2014.05.025
0013-4686/

panel displays based on thin film electroluminescence (TFEL) and semi-conductors industry [11,12]. ALD has already been successfully used to produce to produce functional materials based on ceria or titania for solid oxide fuel cells (SOFC) and MCFC [13,14].

In ALD, pulses of the reactant gases are separately introduced into the reaction chamber where substrates are coated following several steps. 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 determine the film thickness [15]. CeO_2 deposited as a thin film by ALD form compact and crack-free layers, in comparison with other techniques like electrochemical deposition [16–18]. Therefore, the aim of this investigation is to test nanocrystalline CeO_2 deposited by ALD onto a porous nickel substrate as cathode to evaluate its performance as a protective layer for MCFC application by determining its electrochemical behavior in Li_2CO_3-K_2CO_3 (62-38 mol %) under standard cathode atmosphere and its surface changes after 230 h of immersion.

2. Experimental

2.1. CeO_2 layer deposition on porous nickel using ALD

To determine the ALD deposition parameters, thin layers of CeO_2 were processed by ALD over a Si monocrystal oriented in the 111 plane. With the determined parameters, CeO_2 coatings were deposited over commercial porous nickel substrate (produced by Doosan, South-Korea) [19] with the vertical flow type reactor (Picosun SUNALE™ R-series). Four different samples were processed with this technique. A known deposition route was followed using halide-free and non-corrosive Ce(TMHD)$_4$ (tetrakis(2,2,6,6-tetramethyl 1-3,5-heptanedionate Ce(IV)) as precursor for CeO_2 [20,21]. For the Ce(TMHD)$_4$ (Strem Chemicals), ozone was used as oxidizing agent. In order to prepare the CeO_2 layer, Ce(TMHD)$_4$ was sublimated at 180 °C and introduced into the precursor chamber by a N_2 flow of 150 $cm^3\ min^{-1}$ using the following conditions: pulse time 3 s, and purge time 2.5 s. Ozone was supplied at room temperature by a N_2 flow of 100 $cm^3\ min^{-1}$ with pulses of 4 s and purge times of 2.5 s. The reactor temperature was kept at 300 °C in a N_2 flow of 300 $cm^3\ min^{-1}$, the precursor pulse and purge were followed by ozone pulse and purge, this cycle being repeated until the desired thickness was reached. Two different thicknesses were processed with this technique: two samples of 27 nm, and two samples of 127 nm. The samples were named CeO_2-1 and CeO_2-2 for the 27 and 127 nm CeO_2-coated Ni porous cathodes, respectively.

2.2. Electrolyte and cell

The high-temperature electrochemical cell was a single-compartment crucible of dimensions $70 \times 50\ mm^2$ contained in an alumina Al_2O_3 reactor of dimensions $250 \times 60\ mm^2$, hermetically sealed by a stainless steel cover with a Viton O-ring. The whole electrochemical set-up was fully described in a previous paper [22]. Temperature was controlled at a constant temperature of 650 °C by means of a calibrated chromel/alumel thermocouple, the electrolyte was a mixture of lithium and potassium carbonates of high grade purity >98% (Sigma-Aldrich®), in a proportion of 62:38 mol%. The standard cathode atmosphere was a mixture of Air/CO_2 (70:30 mol%) of high grades purity (Air Liquide®) at 650 °C and a pressure of 1 atm. A carbonate melt was prepared and stabilized 24 h at 650 °C for each CeO_2-coated sample. After stabilizing the molten carbonate eutectic under the selected cathode atmosphere, samples were immersed in the carbonate melt and electrochemical measurements were performed for 230 h. After electrochemical tests, 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.

2.3. Electrochemical measurements

To determine the electrochemical performance of the coated samples, a three-electrode system was used, the working electrode being the as-deposited CeO_2-1 and CeO_2-2 on porous nickel substrate of dimensions $10 \times 10 \times 0.5$ mm, the counter electrode was a brand new gold wire of 1 mm diameter (4 cm) and the reference electrode a silver wire dipped into an Ag_2SO_4 (10^{-1} mol kg^{-1}) saturated Li-K carbonate eutectic in an alumina tube sealed by a porous alumina membrane. Electrochemical experimental data were collected using a potentiostat/galvanostat (AutoLab® PGSTAT-302 N). Open Circuit Potential (OCP) was collected for CeO_2-1 and CeO_2-2 samples from 0 to 230 h of immersion. OCP measurements were interrupted periodically to perform electrochemical impedance spectroscopy (EIS). EIS parameters were: scanning frequencies set from 0.001 to 10^6 Hz, with 11 points per decade and signal amplitude of 5 mV respecting the system linearity. After each EIS test, OCP measurements were restarted. This procedure was performed for 230 h with EIS performed at regular intervals.

2.4. Characterization

2.4.1. Characterization of deposited CeO_2 layer on porous Ni by ALD

The CeO_2 layers were characterized by X-ray diffraction, XPS and SEM-EDS. XRD was performed in a PANalyticalX'pert Pro from Anton Paar with Cu–Kα1 radiation (λ=1.54056 Å). The diffraction pattern was obtained by scanning between 20 and 80° by steps of 0.02 (2θ°) with a fixed counting time of 2.3 s and sample rotation of 3 rpm. Once the data were obtained, Scherrer analysis calculation was used to obtain the average crystal size of the deposited layer by determining the angular position and FWHM of the peaks between 28 and 60 2θ degrees. Scanning Electron Microscopy (SEM) and Energy Dispersion Spectroscopy (EDS) analyses were performed with a ZEISS® Ultra 55 microscope to evaluate the surface morphology and to measure layer thicknesses. Raman spectra were obtained for samples of Ni porous coated with CeO_2 in a Lab Raman HR-800 from Horiba Jobin Yvon spectrometer with a spectral resolution of 2 cm^{-1} and Olimpus BX41 microscope using a 50X objective lens to focus the laser beam on the sample. Spectra were recorded from 100 to 1800 cm^{-1} with a He-Ne laser of wavelength 532.07 nm and grid of 600, filter D 0.3, hole of 200 μm, slit of 100 μm. Spectrometer calibration was performed with Si (1 1 1). The X-ray photoelectron spectra were recorded using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with a monochromator Al Kα X-ray ($h\nu$ = 1486.61 eV) for sample excitation. An argon ion beam was used to prevent samples surface charging. The spectrometer energy calibration was obtained using Au 4f 7/2 and Cu 2p 3/2 photoelectron lines. The position of the adventitious carbon C 1s peak at 284.6 eV was used as an internal reference in each sample to determine the binding energies with an accuracy of ± 0.1 eV. The residual pressure in the analysis chamber was maintained below 1×10^{-8}