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Investigation on niobium oxide coatings for protecting and enhancing the performance of Ni cathode in the MCFC

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ABSTRACT

This study addresses the problem of the nickel cathode dissolution, decreasing the lifetime of molten carbonate fuel cells, by a protective coating of Nb₂O₅ processed by atomic layer deposition ALD onto the porous cathode substrate. Samples of different thicknesses were tested electrochemically in molten Li₂CO₃-K₂CO₃ eutectic at 650 °C during 230 h by means of chronopotentiometry and electrochemical impedance spectroscopy. A significant decrease in the stabilization time with respect to the oxygen reduction potential is observed with niobium coatings, which could indicate an electrocatalytic process favoured by the presence of Nb. The structure and morphology of the coated samples are characterised by XRD, SEM and XPS before and after the electrochemical tests. Mixed lithiated Ni and Nb oxides are likely to be formed at the cathode surface. Interestingly, this Nb-containing mixed oxide not only can protect Ni cathode but also maintains its good performance.

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Introduction

There are several types of fuel cells available commercially, each one aims at satisfying a specific niche of clean generated power, portable, mobile or stationary. Molten carbonate fuel cells (MCFC) are better suited for large-scale stationary generation of several MW, more than any type of fuel cell in the

market. MCFC device does not use any precious metal as catalyst making it cheaper to manufacture. Hence, MCFC is an interesting technology for producing clean energy from hydrocarbons, biogas or hydrogen-rich fuels.

The most common material used as MCFC cathode material is nickel, which undergoes *in situ* oxidation and lithiation in the carbonate melt, then nickel starts dissolving and, after reacting with hydrogen, might precipitate as

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metallic nickel onto the anode, causing a short-circuit between both electrodes through the electrolyte [1,2]. One of the best solutions is to deposit a protective coating of a selected metal oxide onto the cathode. There are many studies dedicated to this approach in the literature, sol-gel, electrochemical deposition, chemical vapour deposition, plasma and laser sputtering of various metal oxides. For instance, CeO_2 , TiO_2 , Co_3O_4 , Fe_2O_3 , and mixtures of those have been studied with some significant results [3–10]. Nevertheless, even though addition of such layers decreases Ni solubility, they may also increase the cathode resistance and drop the cathode electrochemical performance. In recent studies, we have used atomic layer deposition (ALD), technique which allows processing ultra-thin and conformal layers, e.g. CeO_2 , TiO_2 , Co_3O_4 , in order to maintain the electrocatalytic properties of the porous nickel substrate [11–13]. Interesting results were obtained, but there is still a need of more performing coatings, combining a protective role and electrocatalytic properties. Niobium compounds and, in particular oxides, are well known for their catalytic properties for oxidation processes; for instance, E. Heracleus et al. and A. Qiao et al. have used Ni-Nb-O and Ni-Nb-M-O compounds for catalysing the oxidative dehydrogenation of ethane reaction, explaining the increased activity of the Ni-O catalyst by the increased surface acidity conferred by Nb species at the surface [14–16]. Nevertheless, other authors have analysed the properties of niobium oxides for reduction processes. A. Takagaki et al. and R. Ohnishi et al. evaluated the performance of niobium oxides as catalysts for oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFC) with good results [17,18]. As far as we know there are no specific mechanistic studies on niobium oxides grown on nickel oxide substrates [19,20]; however, pre-oxidised nickel-niobium alloy has already been suggested by Fang et al. as novel candidate material for replacing the classical nickel oxide cathode [21,22]. These authors obtained a significant drop in Ni solubility (8×10^{-6} instead of 17×10^{-6} mol fraction). They also mentioned that niobium oxide cannot be thermodynamically reduced by H_2 or CO in the anode MCFC atmosphere, which is favourable to the application because no metallic niobium would be deposited in the electrolyte.

In the present study, we investigated for the first time the structural, morphological and electrochemical behaviour of ALD-processed thin layers of different thicknesses of Nb_2O_5 onto the commercial porous Ni cathode. ALD is a chemical gas phase deposition technique first developed in Finland in the 1970s by T. Suntola et al. [23,24]. In ALD, reactant gas pulses are introduced separately in order to reach the substrates to be coated and growth is achieved through self-terminating surface reactions, which means that only one monolayer of reactant gas species can be adsorbed to the surface during a pulse. We worked in Li_2CO_3 - K_2CO_3 bulk at 650°C in conditions simulating MCFC cathode operation. Our aim here is to show whether ALD-processed niobium oxide coatings could play a protective role with respect to Ni cathode and maintain or improve the electrocatalytic properties of nickel. A deeper insight contemplating the mechanistic effect of niobium with respect to oxygen reduction kinetics is out of the scope.

Experimental

Atomic layer deposition of Nb_2O_5

A thin layer of Nb_2O_5 was deposited on a commercial porous nickel substrate (produced by Doosan Company, South-Korea) by means of ALD technique using a vertical flow type reactor (Picosun SUNALE™ R-series). Niobium ethoxide, $\text{Nb}(\text{OCH}_2\text{CH}_3)_5$ (Sigma-Aldrich®) was used as precursor and distilled water as oxidizing agent. In order to process the Nb_2O_5 layer, $\text{Nb}(\text{OCH}_2\text{CH}_3)_5$ was introduced into the precursor chamber using the following conditions: precursor pulse time 0.5 s, purge time 3 s, N_2 line flow of $100 \text{ cm}^3 \text{ min}^{-1}$, water pulse time 0.1 s, purge time 3 s [25]. The precursor was sublimated at 80°C and the water vapour was supplied at 25°C . The reactor temperature was kept at 300°C with a N_2 flow of $300 \text{ cm}^3 \text{ min}^{-1}$, the precursor pulse and purge was followed by water pulse and purge, this cycle was repeated until the desired thickness was reached. The growth rate of Nb_2O_5 layers over the porous nickel substrate was $\approx 1 \text{ \AA/cycle}$. Four different samples were processed by this technique to obtain 5, 20, 50 and 300 nm deposited layers.

Material characterization

Deposited layers were characterized by X-ray diffraction, SEM and XPS. XRD was performed in a PANalytical X'pert Pro from Anton Paar with $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The diffraction pattern was obtained by scanning between 20 and 120° by steps of $0.02 (2\theta^\circ)$ with a fixed counting time of 2.3 s in razing mode. Once the data were obtained, Scanning Electron Microscopy (SEM) analysis were performed with a ZEISS® Ultra 55 microscope to evaluate the surface, morphology and to measure the layer thickness. X-ray photoelectron spectra were recorded using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with a monochromator Al $\text{K}\alpha$ X-ray ($h\nu = 1486.61 \text{ eV}$) for sample excitation. An argon ion beam was used to prevent sample 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 $\pm 0.1 \text{ eV}$. The residual pressure in the analysis chamber was maintained below 10^{-8} Torr, during data acquisition. Three samples of 50 nm niobium oxides deposited on porous nickel were analysed, one as-deposited and two others M1 and M2 after immersion in molten carbonate eutectic at 650°C for 44 h and 144 h respectively. The survey spectrums were obtained between 0 and 1000 eV, for all samples. The spectra were collected and analysed with Advantage 4.0 software.

Electrochemical cell

Lithium and potassium carbonates, of high-grade purity $>98\%$ (Sigma-Aldrich®), were mixed in a proportion of 62:38 mol %. The high-temperature electrochemical cell was a single-compartment crucible of dimensions $70 \times 50 \text{ mm}^2$ contained in an alumina Al_2O_3 reactor of dimensions $250 \times 60 \text{ mm}^2$

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