Supercritical fluid deposition of compositionally uniform yttria stabilized zirconia films

Quentin Le Trequesser [a,b], David Mesguich [b], Eunyoung You [b,c], Cyril Aymonier [a], James J. Watkins [b,*]

[a] CNRS, Université de Bordeaux, ICMCB, 87 Avenue du Dr A. Schweitzer, 33608 Pessac Cedex, France
[b] Polymer Science and Engineering Department, University of Massachusetts-Amherst, 120 Governors Drive, Amherst, MA 01003, USA
[c] Chemical Engineering Department, University of Massachusetts-Amherst, 686 North Pleasant Street, Amherst, MA 01003, USA

ABSTRACT

We report the formation of yttria stabilized zirconia (YSZ) thin films by supercritical fluid deposition (SFD) in carbon dioxide at 20 MPa and a stage temperature of 300 °C via hydrolysis of zirconium(IV) hexafluoroacetylacetonate and yttrium(III) hexafluoroacetylacetonate. Post-deposition annealing of the films at 800 °C yields crystalline films having the expected fluorite structure as evidenced by X-ray diffraction. Such films are suitable for the fabrication of electrolyte thin films for micro-solid oxide fuel cells (μ-SOFC). We show that a cyclic co-deposition process in which aliquots of precursor are introduced sequentially enables the depostion of YSZ thin films with uniform composition as evidenced by X-ray photoelectron spectroscopy. In each cycle, the mixed precursor solution in CO_2 is introduced to the reactor and then purged following a short reaction interval. By contrast, simple batch SFD processes that employ hydrolysis of the mixed precursors introduced at the onset of the depositions lead to non-uniform distributions of the cations throughout the thickness of the films. The cyclic deposition approach extends supercritical fluid deposition to materials such as multi-cations oxides for which precise control of stoichiometry is required.

© 2011 Published by Elsevier B.V.

1. Introduction

The development of efficient alternative energy sources is both timely and important. Solid oxide fuel cells (SOFC) offer several advantages over conventional energy sources, including control of power, good efficiency and the absence of harmful emissions [1–3]. Yttria stabilized zirconia (YSZ) is the state of the art electrolyte material in SOFC due to the high O^{2-} ionic conductivity of the fluorite crystal structure at high temperature [4,5]. However, the high operating temperature (900–1000 °C) of these devices causes mechanical and chemical stability issues, neccesitating the use of expensive materials and reducing lifetimes of the cell. In order to make commercialization viable, it is crucial to reduce cost. One means to achieve this is to reduce the operating temperature to around 600 °C and move towards intermediate temperature SOFC (IT-SOFC) [6]. Thin film components are attractive for integration into these devices, especially in the field of micro SOFC (μ-SOFC). μ-SOFC are under development for applications in portable electronics such as laptops, cell phones or tablet computers [7–9] for which they offer compact design with higher efficiency at intermediate temperatures. YSZ thin films have been deposited via various methods such as electron beam evaporation [10], pulsed laser deposition [11], and chemical vapor deposition [12]. In this study, we demonstrate a new way to deposit YSZ thin films with controlled composition and thickness using supercritical fluid deposition in carbon dioxide at 15–20 MPa and a stage temperature of 300 °C.

Supercritical fluid deposition (SFD) has proven to be an efficient way to deposit pure metal or metal oxide films at moderate temperature and pressure with exceptional step coverage [13–15]. The suitability of SFD films for SOFC has also been recently investigated [16]. Supercritical fluids offer advantages such as high diffusivity, low viscosity and high precursor concentrations in the fluid phase, which mitigate or eliminate mass transport limitations to deposition rate and provide conformal coverage in high aspect ratio features. In this work, YSZ thin film deposition in supercritical CO_2 ($scCO_2$) was performed in a cold wall reactor (with a stage temperature of 300 °C) using a cyclic precursor flow to obtain homogeneous composition within the film. The approach can be extended to co-depositions of other metals and metal oxides.

2. Material and methods

Zirconium(IV) hexafluoroacetylacetonate ($Zr(hfac)_4$) and yttrium(III) hexafluoroacetylacetonate ($Y(hfac)_3$) were purchased from Strem Chemicals. We developed a cyclic deposition set up

* Corresponding author. Tel.: +1 413 545 2569; fax: +1 413 545 0082.
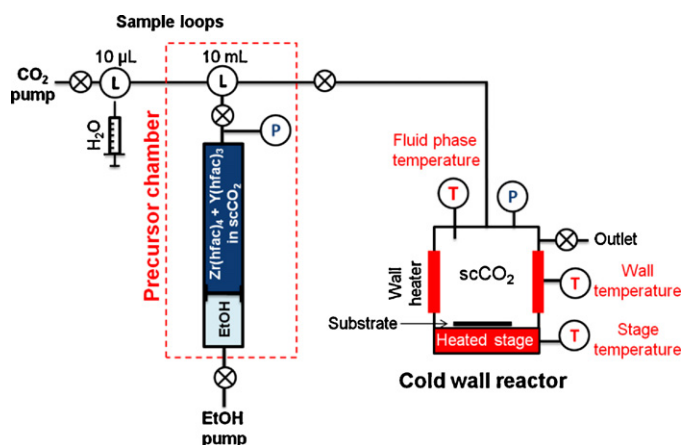*E-mail address:* watkins@polysci.umass.edu (J.J. Watkins).

Fig. 1. Schematic of the cyclic supercritical fluid deposition setup. The 100 mL high pressure reactor is connected via a 10 mL sample loop to the 60 mL precursor chamber where Zr and Y precursors are soaked in scCO$_2$ at 60 °C and 14 MPa.

(Fig. 1) based on the cold wall reactor used to perform standard metal oxide depositions [13], the main difference consisting of the addition of one precursor chamber, wherein the precursors were solubilized in scCO$_2$ to provide a reservoir of precursor solution. The precursor chamber is divided in two sections separated by a piston ring, one containing the precursors in solution in scCO$_2$ and the other containing ethanol. One end of the chamber is connected to a high pressure syringe pump (Teledyne ISCO Inc.) filled with CO$_2$ and to a sample loop used to inject a precise volume (10 mL) of the precursor solution in the reactor. The second end of the chamber is connected to another high pressure syringe pump (Teledyne ISCO Inc.) filled with ethanol. Ethanol is a nearly incompressible fluid at the conditions used and setting the ethanol pump at a certain pressure (14 MPa) ensures that the pressure in both sections of the precursor chamber will remain constant even as the volume of the precursor solution diminishes after each injection cycle.

The solid precursors (0.085 mmol of Zr(hfac)$_4$, 0.2 wt.% in CO$_2$, 0.015 mmol of Y(hfac)$_3$, 0.03 wt.% in CO$_2$) were introduced in the 60 mL precursor chamber subsequently filled with CO$_2$. The precursors were solubilized at 60 °C and 14 MPa (above CO$_2$ critical coordinates) for 60 min. The reactor, a 100 mL stainless steel vessel equipped with a heated stage, was first sealed with the substrate (Si wafer) mounted on the stage and flushed with nitrogen for an hour at 60 °C. The stage temperature was then set to 300 °C while the wall temperature remained set at 60 °C and scCO$_2$ was added until the pressure reached 10 MPa. At the beginning of each cycle, a specific volume (10 mL) of the precursor solution was injected via the sample loop into the cold wall reactor and a small volume of water (10 μL) was injected via the second sample loop to initiate the hydrolysis reaction. The deposition took place at 300 °C and 20 MPa for 10–30 min, H$_2$O/(Zr + Y) molar ratio is 30. At the end of each cycle the reactor was vented to remove by-products and any un-reacted precursors and then filled with scCO$_2$ in preparation for another cycle. The deposition was typically stopped after 5–6 cycles.

Film composition was characterized by X-ray photoelectron spectroscopy (XPS) using a Quantum 2000 scanning ESCA microprobe (Physical Electronics) coupled with an Ar$^+$ ion-sputtering gun and charge neutralizing system. Film thickness was measured with a Veeco Dektak 3 mechanical profilometer. Film crystallinity was characterized by X-ray diffraction (XRD) using PANalytical X'Pert diffractometer (Cu K$_\alpha$ radiation) in 2θ mode with an incident X-ray beam angle fixed at 0.5°, and the detector 2θ angle varying step by step from 25° to 110°.

3. Results and discussion

Brightly colored films were deposited onto the silicon wafers. Film thicknesses, measured by profilometry, varied between 170 and 250 nm depending on the number of cycles. The films showed slight color variations that are attributed to thickness variations [13]. At the reaction conditions studied, each cycle resulted in the deposition of an oxide layer (containing both cations) about 35 nm thick. The thickness of each layer can be controlled by the amount of precursors and water introduced and the reaction time.

Cyclic depositions via SFD were previously reported by Gougousi et al. [17]. Their work, inspired by atomic layer deposition (ALD) processes that rely on a self-limiting surface reaction via alternating monolayers, focused on low temperature (≤100 °C) deposition of single oxides using oxidizers (organic peroxides) to facilitate deposition. Here our objective was not to mimic ALD, but rather to provide a means for controlling or eliminating composition gradients normal to the film surface during SFD depositions that are not self-limiting. The high temperature (300 °C) cyclic co-deposition of metal oxide films via precursor hydrolysis in scCO$_2$ enables precise control of the stoichiometry in the films for mixed depositions in which the inherent deposition rates from the metal oxide precursors differ markedly.

Fig. 2 shows a comparison of XPS sputter depth profiles of YSZ films deposited in identical experimental conditions (300 °C, 20 MPa, H$_2$O/(Zr + Y) molar ratio = 30), albeit one was deposited using a standard batch process (Fig. 2a) and the other was deposited by cyclic deposition (Fig. 2b). A simple batch SFD co-deposition of Y and Zr oxides using a standard (non-cyclic) process leads to significant composition gradients that result from different deposition rates. The XPS profile shows that the atomic concentration of yttrium varies along the film thickness. The Y concentration is high in the vicinity of the substrate (Si wafer) and diminishes until becoming negligible at the surface of the film. On the contrary, Zr concentration is higher at the film surface. This suggests that the hydrolysis of Y precursor to form the oxide (Y$_2$O$_3$) is faster than the hydrolysis of the Zr precursor to yield ZrO$_2$. A second possibility is that the liberated hexafluoroacetylacetone can react with the incipient YSZ surface to selectively etch Zr over Y. However, an experiment exposing a previously deposited YSZ film to hexafluoroacetone in scCO$_2$ in conditions similar to a deposition experiment (300 °C, 20 MPa, 0.385 mmol of hexafluoroacetylacetone, 50 μL of H$_2$O) ruled out this possibility. Indeed the film composition was identical before and after the experiment, no etching was observed. Therefore we attribute the composition gradient in the film to the different hydrolysis rates of the precursors.

Fig. 2b shows XPS results for a film deposited by the cyclic deposition process in which the same quantity of precursor and water as used in batch experiment (Fig. 2a) is introduced using six cycles of 30 min of deposition (compared to a single injection followed by 30 min of deposition for the batch experiment). From the XPS results one can easily notice that each injection cycle is characterized by a rise of Y concentration in the film composition, followed by simultaneous decrease in the Y content and increase in Zr content. This pseudo-sinusoidal evolution of film composition provides verification of the concept: indeed, cyclic injection leads to an overall steadier film composition with Y percentage remaining between 10 and 20%; however, the impact of the difference in reaction kinetics between the precursors is still noticeable. Controlling the number of cycles also allows adjusting the thickness of the films.

Refinement of the experimental process using shorter reaction cycles (10 min instead of 30 min) and slowly injecting the precursor solution as well as water into the reactor resulted in much more uniform film composition as illustrated in Fig. 3b. The film composition is consistent all along the depth of the film as there
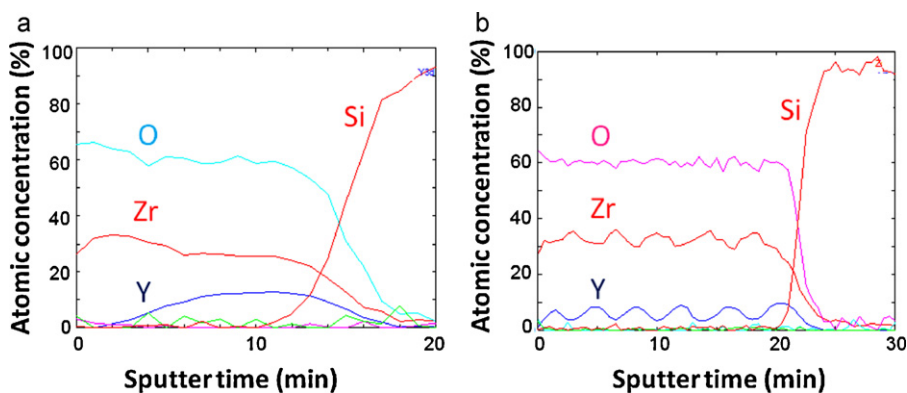
Fig. 2. XPS sputter depth profiles of Y and Zr oxides thin films deposited with the standard (a) and cyclic (b) co-deposition process (after annealing 400 °C).

is no variation in the Zr:Y stoichiometry. The cation stoichiometry is determined experimentally using XPS and found to be 86:14, which is in good agreement with the 85:15 Zr:Y molar ratio introduced in the precursor mixture. Therefore in addition to yielding a uniform film composition, this technique allows fine control of the film composition by adjusting the composition of components in the precursor solution.

The films were then annealed in air at 400 °C for 6 h to remove impurities (carbon and ligand residues). Further annealing at 800 °C for 6 h was required to initiate YSZ crystallization (the as-deposited and annealed at 400 °C films are amorphous). The XRD pattern shown in Fig. 3a indicates the presence of the expected phase: YSZ fluorite type structure (face-centered cubic: Fm-3m, JCPDS 30-1468).

In order to study the effect of precursor concentration on films deposition, another YSZ film was deposited in standard

batch conditions with a precursor concentration 6 times lower (0.0142 mmol of $Zr(hfac)_4$ and 0.0025 mmol of $Y(hfac)_3$) to mimic 1 deposition cycle. Indeed the total amount of Zr and Y precursor was identical for standard and cyclic depositions; the fluid phase precursor concentration during reaction is 6 times higher for standard deposition compared to cyclic deposition with 6 reaction cycles. The corresponding film is about 35 nm thick and XPS analysis (Fig. 4b) does not show evidence of faster deposition of Y compared to Zr. This result suggests that the differences in kinetics become negligible at very low concentrations or precursor, which is consistent with the results obtained for cyclic depositions.

The possibility that high temperature annealing leads to cation diffusion was also investigated. Fig. 4 shows Zr and Y composition profiles of annealed films deposited using the standard batch technique with high (a) and low (b) concentrations and cyclic
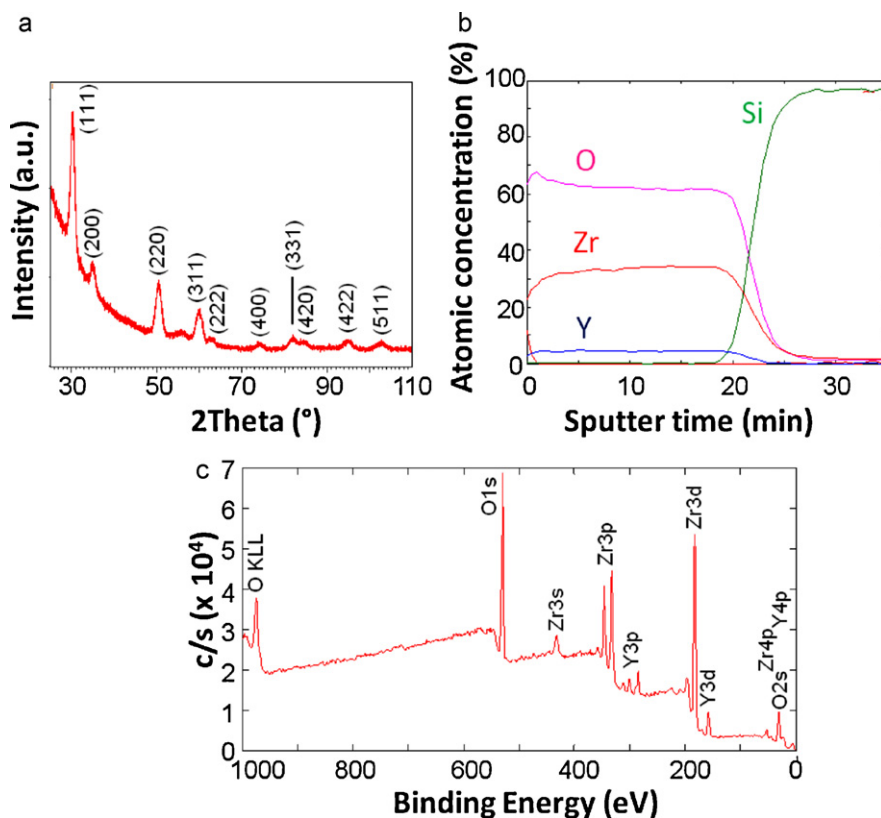

Fig. 3. XRD pattern (a) of a YSZ film (annealed at 800 °C for 6 h), XPS sputter depth profile (b) and XPS energy survey (c) of a YSZ film obtained with 10 min reaction cycles (annealed at 400 °C for 6 h).
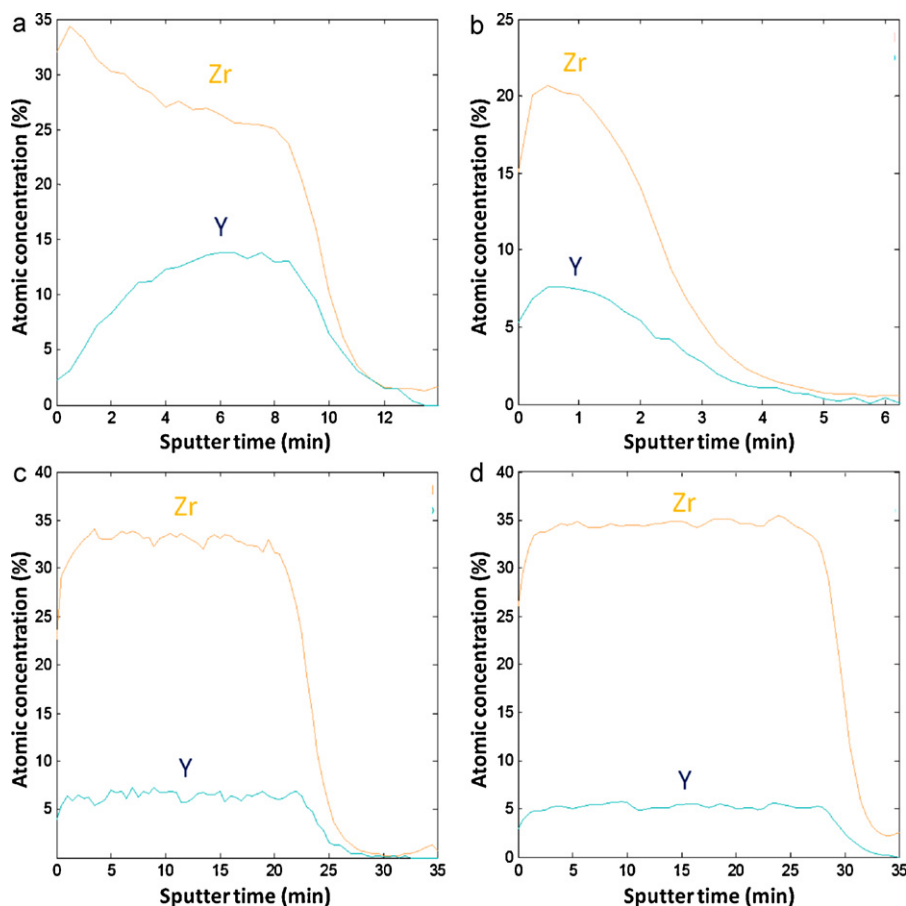
Fig. 4. XPS Zr and Y composition profiles of YSZ films annealed at 800 °C for 6 h (a) standard deposition, (b) standard deposition with low precursor concentration, (c) cyclic deposition with 30 min reaction cycles, (d) cyclic deposition with 10 min reaction cycles. All depositions at 300 °C, 20 MPa from 0.085 mol Zr(hfac)$_4$ and 0.015 mol Y(hfac)$_3$ except (b) from 0.0142 mol Zr(hfac)$_4$ and 0.0025 mol Y(hfac)$_3$.

depositions with 30 min (c) and 10 min (d) cycles. Annealing at 400 °C results in elimination of the carbon content of the film but has no influence on the cation stoichiometry. Annealing at 800 °C has negligible effect on the Zr:Y ratio on all samples with the notable exception of the film deposited with 30 min cycles (Fig. 4c). Instead of the pseudo-sinusoidal evolution of the film composition (see Fig. 2b), Zr and Y remain nearly constant throughout the depth of the film. However, this effect from diffusion is limited and film composition remains slightly less uniform than for the film obtained with 10 min deposition cycles (Fig. 4d). Composition profiles for the samples deposited with the standard approach (Fig. 4a and b) are largely unaffected by the high temperature treatment.

Moreover, the cyclic co-deposition leads to thicker oxide films compared to the standard batch deposition (230 nm and 140 nm respectively at 300 °C, 20 MPa, H$_2$O/(Zr + Y) molar ratio = 30). In fact, injecting the overall same amount of precursors and water in multiple cycles of 10 min instead of injecting all at once for 30 min of reaction achieves better deposition rate. Water is injected along with the precursors at the beginning of each cycle which ensures a constant presence of water to react with the precursors; precursor concentration during the hydrolysis reaction in humidified CO$_2$ is lower and by-products and un-reacted precursors are flushed out of the reactor between each cycle which provides optimized conditions for further reaction cycles. Short deposition cycles are also likely to stop the reaction in its early phase when homogeneous deposition is easier to achieve (see Fig. 2a in which the film composition nearly stays constant close

to the surface of the substrate, especially compared to the outer part of the film which is rich in Zr and poor in Y because there is only Zr left to react in the end of the batch experiment).

As a result, we believe cyclic deposition of oxides with controlled stoichiometry opens the field of SFD to new applications such as µ-SOFC. The film quality associated with this low-temperature technique coupled with precise control of the stoichiometry via cyclic deposition make it a suitable technique for the deposition of dense ionic conductor oxide films. Those co-depositions have to be further studied in the future, to evaluate the effect of film composition and film thickness and to assess the electrochemical behavior of such thin films.

4. Conclusions

In summary, SFD is an efficient means for the deposition of a multi-component oxide thin film. In this paper we demonstrated the efficiency of the cyclic deposition towards well-controlled film composition, illustrated by the co-deposition of YSZ films with definite Zr:Y stoichiometry as a model system. The technique constitutes a useful alternative to the existing methods to deposit high quality metal oxide films and could be used in the future to create high efficiency µ-SOFCs. More generally, cyclic deposition provides a solution to the differences in deposition kinetics and could be extended to other systems enabling the deposition of multi-component materials which could not previously be deposited by SFD.

Acknowledgment

References

[1] D. Beckel, A. Bieberle-Hütter, A. Harvey, A. Infortuna, U. Muecke, M. Prestat, J. Rupp, L. Gauckler, Thin films for micro solid oxide fuel cells, J. Power Sources 173 (1) (2007) 325–345.

[2] A. Bieberle-Hütter, D. Beckel, A. Infortuna, U.P. Muecke, J.L. Rupp, L.J. Gauckler, S. Rey-Mermet, P. Muralt, N.R. Bieri, N. Hotz, M.J. Stutz, D. Poulikakos, P. Heeb, P. Müller, A. Bernard, R. Gmür, T. Hocker, A micro-solid oxide fuel cell system as battery replacement, J. Power Sources 177 (1) (2008) 123–130.

[3] J. Fleig, Microelectrodes in solid state ionics, Solid State Ionics 161 (3–4) (2003) 279–289.

[4] T.H. Etsell, S.N. Flengas, Electrical properties of solid oxide electrolytes, Chemical Reviews 70 (3) (1970) 339–376.

[5] B.C.H. Steele, A. Heinzel, Materials for fuel-cell technologies, Nature 414 (6861) (2001) 345–352.

[6] Z. Shao, S.M. Haile, A high-performance cathode for the next generation of solid-oxide fuel cells, Nature 431 (7005) (2004) 170–173.

[7] H. Huang, M. Nakamura, P. Su, R. Fasching, Y. Saito, F.B. Prinz, High-performance ultrathin solid oxide fuel cells for low-temperature operation, J. Electrochemical Society 154 (1) (2007) B20–B24.

[8] S.J. Litzelman, J.L. Hertz, W. Jung, H.L. Tuller, Opportunities and challenges in materials development for thin film solid oxide fuel cells, Fuel Cells 8 (5) (2008) 294–302.

[9] A. Evans, A. Bieberle-Hütter, H. Galinski, J. Rupp, T. Ryll, B. Scherrer, R. Tölke, L. Gauckler, Micro-solid oxide fuel cells: status, challenges, and chances, Monatshefte für Chemie/Chemical Monthly 140 (2009) 975–983.

[10] M. Hartmanova, K. Gmucova, I. Thurzo, Dielectric properties of ceria and yttria-stabilized zirconia thin films grown on silicon substrates, Solid State Ionics 130 (1–2) (2000) 105–110.

[11] D. Fork, D. Fenner, G. Connell, J. Phillips, T. Geballe, Epitaxial yttria-stabilized zirconia on hydrogen-terminated Si by pulsed laser deposition, Applied Physics Letters 57 (11) (1990) 1137–1139.

[12] Z. Xu, S. Yarmolenko, J. Sankar, Exploration of combustion cvd method for ysz thin film electrolyte of solid oxide fuel cells, Fuel Cell Technologies: State and Perspectives 202 (2005) 49–57.

[13] A. O'Neil, J. Watkins, Reactive deposition of conformal metal oxide films from supercritical carbon dioxide, Chemistry of Materials 19 (23) (2007) 5460–5466.

[14] J. Blackburn, D. Long, A. Cabañas, J. Watkins, Deposition of conformal copper and nickel films from supercritical carbon dioxide, Science 294 (5540) (2001) 141–145.

[15] A.H. Romang, J.J. Watkins, Supercritical fluids for the fabrication of semiconductor devices: emerging or missed opportunities? Chemistry Reviews 110 (1) (2010) 459–478.

[16] D. Mesguich, C. Aymonier, J.-M. Bassat, F. Mauvy, E. You, J.J. Watkins, Low-temperature deposition of undoped ceria thin films in scCO$_2$ as improved interlayers for it-sofc, Chemistry of Materials, doi:10.1021/cm2012846.

[17] T. Gougousi, D. Barua, E.D. Young, G.N. Parsons, Metal oxide thin films deposited from metal organic precursors in supercritical CO$_2$ solutions, Chemistry of Materials 17 (20) (2005) 5093–5100.