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Title: Exploring stable and selective anode materials for the electrochemical oxidative coupling of methane (EOCM): a case study of doped titanates

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The electrochemical oxidative coupling of methane (EOCM) is an emerging process through which methane can be converted into value-added products such as ethylene. However, this application is hampered by the fact that a stable and ethylene-selective anode material does not currently exist. In this study, we analyse a selection of titanate-based anode materials: SrTi_{0.3}Fe_{0.63}Co_{0.07}O₃, SrTi_{0.65}Fe_{0.35}O₃ and La_{0.3}Sr_{0.7}TiO₃. We analyse the stability of these materials under EOCM operating conditions using post-mortem characterisations involving XRD, XPS and EDS analyses. We also characterise the ethylene production of these anode materials at similar current densities. We find that Fe/Co-doped titanates are unstable under EOCM conditions and undergo significant phase decomposition while La_{0.3}Sr_{0.7}TiO₃ remains stable over several weeks of operation.

Introduction

Ethylene (C_2H_4) is one of the most valuable compounds in the chemical industry as it is used as a building block for a wide range of applications. The current ethylene production pathway via steam cracking of naphtha or ethane is highly endothermic, meaning that ethylene production is the second-biggest CO₂-generating process in industry.¹ In 1982, Keller and Bhasin first reported on an alternative ethylene production pathway,² the oxidative coupling of methane (OCM). In this approach, CH₄ is oxidised by adsorbed O₂-derived species on oxide catalyst surfaces, forming CH₃⁻ radicals which can then recombine in the gas phase to yield C₂H₆, which is further oxidised to yield the desired C₂H₄ and by-product H₂O. While the literature is replete with OCM studies, a fundamental challenge is a lack of catalysts which can achieve both high C₂ (C₂H₆ and C₂H₄) selectivity and high C₂ yield.³ The conventional OCM approach suffers from significant "deep oxidation" where CH₄ is instead combusted to form CO/CO₂ and H₂O: this arises as the products of oxidative coupling are more reactive towards deep oxidation than the parent CH₄.

With a view towards improving the C₂ selectivity and yield of OCM processes, recent works have focused on integrating OCM activity into typical solid oxide electrolyzer systems. In this electrochemical OCM (EOCM) approach, O^{2-} ions from the cathode side are transported across the electrolyte to the anode where they oxidise CH₄ molecules to yield CH₃⁻ radicals: a schematic of this approach is presented in Figure 1.





The benefit of this approach is that CH₄ can be activated more selectively not only by tuning the incoming O²⁻ ion flux but also by tuning the applied potential: when coupled with renewable sources of energy, this process has the potential for reducing the CO₂ footprint of ethylene production. However, while recent publications have claimed exceptional C₂ selectivities of >80-90%, this has become controversial. For example, a recent analysis⁴ found that a previously studied material, Sr₂Fe_{1.5}Mo_{0.5}O₆₋₆, exhibited a strong tendency for deep oxidation and also a strong propensity for coking and phase decomposition. The goal is therefore to investigate anode materials that are mixed conductors for both O²⁻ ions and electrons, and also catalyse the OCM reaction to produce C₂'s selectively, while remaining stable over extended periods of operation. The issue here is that historically these properties seemed to be mutually exclusive. Materials that are active for conventional OCM include basic oxides⁵ such as La₂O₃ or SrO which are electronically and ionically insulating. On the flip side, mixed ionic-electronic conductors such as La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ are active for deep oxidation. Therefore, we must balance the electrode material composition to provide adequate electrochemical properties but still facilitate OCM.

We propose that titanate-based systems, derived from the parent $SrTiO_3$, are ideal candidates. Titanates are stable over 1000's of hours of SOFC operation⁶ and $SrTiO_3$ is also known to be a moderately selective catalyst for OCM.⁷ In this study, we use state-of-the-art anode materials: $SrTi_{0.3}Fe_{0.63}Co_{0.07}O_3$,⁸ $SrTi_{0.65}Fe_{0.35}O_3$ ⁹ and $La_{0.3}Sr_{0.7}TiO_3$ ¹⁰ and evaluate their EOCM activity and material stability.

Experimental

Materials preparation

All doped titanates very synthesised using a combustion sol-gel procedure from an aqueous solution. 10mL of 70% HNO₃ was added slowly to 10mL of water to create an acidic solution. Then, the desired amount of $Ti(C_4H_9O)_4$ was dissolved in the solution under constant stirring. Then, the desired additional cations were added as nitrate salts (La(NO₃)₃·6H₂O, Sr(NO₃)₂, Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O), also under constant stirring. Citric acid in a 1.3:1 ratio with the cations was added to the solution which was then heated to ~60°C at which point NH₄OH was

added to the solution drop-wise until the solution pH reached 6. Then, ethylene glycol in a 1:1 ratio with the citric acid was added dropwise to the solution. The solution was then heated, forming a gel which dried with heating and then underwent self-combustion. The resulting loose debris was collected into an alumina crucible and heated to 350°C for 4hrs and 1050°C for 5hrs.

Materials characterisation

XRD patterns were collected either using a Panalytical Empyrean diffractometer (Malvern Panalytical) equipped with a Mo source and a Galipix 3D detector, or a Bruker D8 Advance General Area Detector Diffraction System (GADDS) equipped with a Co source and a VÅNTEC-2000 detector: data collected with a Co anode have been converted into their Mo equivalents. XPS measurements were made using a Perkin-Elmer PHI-5500 ESCA spectrometer equipped with a monochromated Al K_{α} X-ray at an emission angle of 45°. Electrochemical measurements were performed using a Ametek PARSTAT 4000A workstation. EDS analyses were performed using a Zeiss Merlin High-Resolution SEM equipped with an energy-dispersive X-ray fluorescence spectrometer (EDS, EDAX Octane Elite EDS).

Cell fabrication

To prevent Sr diffusion into the zirconia-based electrolyte, barrier layers of Ce_{0.8}Gd_{0.2}O₂ (GDC from fuelcellmaterials, a Nexceris company) were deposited on scandia-stabilised zirconia electrolytes (Hionic-2.0, fuelcellmaterials) via screen printing. The GDC powder was mixed in a 1.33:1 ratio with a commercial ink vehicle (fuelcellmaterials) and then ground in a mortar and pestle until homogenously incorporated. Then, the ink was printed onto the zirconia electrolytes. Following air drying, the GDC-printed electrolytes were sintered at 1350°C for 5hrs. To print the electrode materials, the calcined powders were ground in a mortar and pestle with the ink vehicle in a 1.75:1 powder:vehicle ratio, printed onto the GDC layer, dried in air and then sintered at 1150°C for 2hrs.

Measurement setup

A schematic diagram of the reactor setup is shown in Figure 2. The anode and cathode were connected by painting a small grid of Au paint (fuelcellmaterials) directly onto the electrode. While the paint was still wet, an Au mesh (Fiaxell SOFC Technologies) was applied to the cell, pressed into the Au paint and then the cell was sintered at 900°C for 1hr to fix the electrode contacts. The exposed electrode area is typically ~0.5cm². For testing, the cell was mounted into an alumina holder and then sealed with a glass sealant, followed by slow heating in a furnace to the desired temperature (800°C). Air was fed to the cathode at a rate of 50sccm and CH₄/Ar mixtures were fed to the anode at a rate of 100sccm. The outlet gas compositions were analysed using a micro GC (Agilent Technologies 990 Micro GC).



Figure 2. Schematic diagram of the EOCM reactor.

Quantitative treatments

The typical figure-of-merit for OCM studies is the C₂ selectivity:

$$C_{2} selectivity = \frac{2(\dot{n}_{C_{2}H_{6}}^{out} + \dot{n}_{C_{2}H_{4}}^{out} + \dot{n}_{C_{2}H_{2}}^{out})}{\dot{n}_{CH_{4}}^{in} - \dot{n}_{CH_{4}}^{out}}$$

where \dot{n}_i^{in} is the concentration of species *i* at the inlet and \dot{n}_i^{out} is the concentration of species *i* at the outlet. However, we found significant coke deposition on the reactor walls after the measurements were completed. Therefore, to provide a fairer evaluation of the EOCM activity of our anode materials, we instead use the C₂/CO_x ratio:

$$C_2/CO_x = \frac{2(\dot{n}_{C_2H_6}^{out} + \dot{n}_{C_2H_4}^{out} + \dot{n}_{C_2H_2}^{out})}{\dot{n}_{CO_2}^{out} + \dot{n}_{CO}^{out}}$$

Since the CH₄ conversion does not feature in this metric, it is a more representative figure for the EOCM activity of an analysed material in the presence of coking.

Results and Discussion

Characterisation of material stability

Material #1: SrTi_{0.3}Fe_{0.63}Co_{0.07}O₃ (STFCo)

Figure 3(a) shows the XRD pattern of STFCo powder. The desired phase has been identified in the as-prepared (calcined) powder, indicating that the perovskite phase was successfully obtained.



Figure 3. XRD pattern of (a) the as-prepared $SrTi_{0.3}Fe_{0.63}Co_{0.07}O_3$ powder and (b) the postmortem $SrTi_{0.3}Fe_{0.63}Co_{0.07}O_3$ cell.

Post-mortem characterisation was carried out using XRD. As shown in Figure 3(b), the XRD pattern of the cell after testing under EOCM conditions reveals the presence of additional phases not present for the as-prepared powder in Figure 3(a). We identify these additional species as $SrCO_3$ and Fe_2CoO_4 (however $FeCo_2O_4$ also matched closely). The presence of segregated oxides instead of the expected perovskite phase indicates that the material is very unstable under EOCM conditions and undergoes significant phase decomposition.

Since the surface is the active region of the anode, we characterised the surface composition using XPS. As shown in Figure 4(a), the Ti signal is present for the cathode but completely absent for the anode. Conversely, as seen in Figure 4(b), both the anode and cathode display very similar signals for the Fe 2p region, indicating that Fe is still present at the surface. This data suggests that STFCo undergoes a preferential segregation of Fe to the electrode surface. It is likely that, similar to the phenomenon of exsolution,¹¹ the ability of Fe³⁺ to be reduced all the way to Fe⁰ is a thermodynamic driver for the decomposition. Additionally, as in Figure 4(c), we find that a significant CO_3^{2-} peak is present in the C 1s spectrum, further indicating decomposition of the electrode material. We attribute this enhancement in CO_3^{2-} concentration to the formation of SrCO₃ as seen in the XRD data (Figure 3(b)) and in the XPS data for the Sr 3d region seen in Figure 4(d). The enhanced features in the Sr 3d spectrum seen at higher energy are typical of surface-



like Sr species,¹² and this observation suggests that the electrode surface has a strong preference for SrCO₃: since this is an electronic and ionic insulator, SrCO₃ passivates the electrode surface.

Figure 4. XPS analysis of the post-mortem SrTi_{0.3}Fe_{0.63}Co_{0.07}O₃ cell showing the (a) Ti 2p, (b) Fe 2p, (c) C 1s and (d) Sr 3d regions.

To visualise this phase decomposition, we used EDS mapping of regions of the electrode surface. As shown in Figure 5(c, d), the Sr and O distributions are relatively uniform over the entire electrode surface, providing further indication that SrO/SrCO₃ is the dominant surface termination. Looking at the Fe and Ti distributions in Figure 5(b, e), we see highly non-uniform distributions with significant segregation of the constituent elements. This provides further evidence for the instability of STFCo as an anode material for EOCM.



Figure 5. (a) Representative SEM image of the post-mortem SrTi_{0.3}Fe_{0.63}Co_{0.07}O₃ surface. EDS mappings of the (b) Fe distribution, (c) Sr distribution, (d) O distribution and (e) Ti distribution.

Material #2: SrTi_{0.65}Fe_{0.35}O₃ (STF)

Since Fe was strongly segregating to the near-surface of STF, we hypothesised that reducing the Fe content of the titanate system might lead to a more stable anode material. Therefore, we synthesised STF and confirmed its phase via XRD: the pattern was very similar to that seen in Figure 3(a), so we do not reproduce it here.



Figure 6. (a) Representative SEM image of the post-mortem $SrTi_{0.65}Fe_{0.35}O_3$ surface. EDS mappings of the (b) Fe distribution, (c) Sr distribution, (d) O distribution and (e) Ti distribution.

We tested the cell for a very short time under the EOCM anode environment, approx. 4 days, and applied a maximum of 8mA to the cell. However, STF also exhibited strong phase decomposition as evident in XRD and XPS, similar to the data shown in Figures 3-4. To illustrate the electrode decomposition, in Figure 6 we show EDS mappings of the elemental distributions. Again, we see an abundance of Sr at the surface (Figure 6(b)) and the Fe signal shows an appreciable degree of elemental segregation for this electrode material as shown in Figure 6(c). However, the Ti mapping in Figure 6(d) does not show the same extent of Ti segregation, highlighting that the Fe content is a key driver for phase decomposition of the electrode. However, STF is still not acceptable for stable EOCM as we only used 5% CH₄ in Ar and polarised to small currents only. Higher CH₄ concentrations and higher currents would likely lead to more phase decomposition, negating the usefulness of this material for EOCM.

Material #3: La0.3Sr0.7TiO3_(LST)

Since reducing the Fe content of the titanate seemed to improve the electrode stability, we decided to remove Fe from the material entirely. LST is a known stable anode for fuel cells and so we decided to apply it directly to our EOCM reactor. While LST has been studied previously for EOCM, the material stability was not characterised.¹³ We used LST as the anode in a reactor that operated for >2 weeks at 800°C under both low currents and high currents. In Figure 7(a), we show the XRD pattern of the as-prepared LST powder.



Figure 7. XRD pattern of (a) the as-prepared $La_{0.3}Sr_{0.7}TiO_3$ powder and (b) the post-mortem $La_{0.3}Sr_{0.7}TiO_3$ cell.

We obtained a 30% La phase with some small amounts of TiO_2 impurities. In Figure 7(b), we show the XRD pattern of the post-mortem LST cell. This XRD pattern is nearly identical to that seen for the as-prepared LST powder as shown in Figure 7(a). This is the first indication of true material stability under EOCM conditions.

XPS characterisation of the LST surface chemistry is shown in Figure 8. As evidenced by the C 1s signal in Figure 8(a), certain regions of the LST surface show large concentrations of saturated-like carbon, typically attributed to coking in high temperature anodes using CH₄. We did indeed see coke (visual inspection) on the LST surface post-mortem, however it is not currently clear whether this coke formed during reactor operation or during cooling in the same anode gas environment. Nevertheless, we do not observe a significant carbonate feature in the XPS data, signifying that LST is stable against carbonate deposition. The Ti 2p data seen in Figure 8(b) also indicate that Ti is indeed stable at the LST surface even in post-mortem samples. Therefore, we believe that the removal of Fe/Co from the anode composition leads to enhanced stability of the electrode under EOCM operational conditions. The Sr 3d data (not shown) likewise displayed a reduced tendency for Sr segregation as compared to Fe/Co-doped systems, highlighting once again the superior stability of LST.



Figure 8. XPS analysis of the post-mortem $La_{0.3}Sr_{0.7}TiO_3$ cell showing the (a) C 1s and (b) Ti 2p regions.

Finally, the EDS mappings in Figure 9 of the post-mortem LST cell show that all elements are uniformly distributed across the sample. Therefore, LST has been shown to be stable under EOCM operating conditions for extended periods of time, serving as a promising anode material for EOCM.



Figure 9. (a) Representative SEM image of the post-mortem $La_{0.3}Sr_{0.7}TiO_3$ surface. EDS mappings of the (b) La distribution, (c) Sr distribution, (d) O distribution and (e) Ti distribution.

Characterisation of EOCM activity

In Table 1 we characterise the C_2/CO_x ratio for STFCo and LST. We see that LST is far superior to STFCo for producing the desired C_2 species such as C_2H_4 . We attribute this difference to the absence of Fe/Co from the anode which are known to be efficient catalysts for complete combustion of CH₄ in conventional fuel cell applications. Therefore, by carefully selecting the constituent elements, we have demonstrated the ability to fine tune the EOCM activity of the anode.

Table 1. Characterisation of EOCM performance of cells studied thus far. Conditions: 800°C,100% CH4 fed to the reactor, 100mA current drawn for $La_{0.3}Sr_{0.7}TiO_3$ and 109mA current drawnfor $SrTi_{0.3}Fe_{0.63}Co_{0.07}O_3$.

Material	C ₂ /CO _x ratio
SrTi _{0.3} Fe _{0.63} Co _{0.07} O ₃	8.4%
La _{0.3} Sr _{0.7} TiO ₃	26.3%

Conclusions

In this study, we have analysed the materials stability of anodes for EOCM under various gas and polarisation conditions. We have demonstrated that Fe/Co-doped titanates are unstable under EOCM conditions, with significant segregation of the constituent elements evident in post-mortem analyses. Therefore, we propose that a key design principle for selecting good EOCM anodes is to remove elements which have several easily accessible redox states (e.g. Fe, Co), as

the reducing environment of the anode will create a thermodynamic driver for phase decomposition of the anode. Since Fe/Co are usually highly desirable for their electrochemical properties, selecting anodes for EOCM involves carefully balancing the electrochemical efficiency with the material stability. Further, Fe/Co doping leads to an enhanced propensity for deep oxidation to CO/CO₂, showing that the requirements of EOCM necessitate a careful choice of the constituent elements beyond just choosing elements which have the highest electrochemical activity.

References

(1) Rightor, E. G.; Tway, C. L. Global energy & emissions reduction potential of chemical process improvements. *Catalysis Today* **2015**, *258*, 226-229. DOI:

https://doi.org/10.1016/j.cattod.2015.02.023.

(2) Keller, G. E.; Bhasin, M. M. Synthesis of ethylene via oxidative coupling of methane: I. Determination of active catalysts. *Journal of Catalysis* **1982**, *73* (1), 9-19. DOI: <u>https://doi.org/10.1016/0021-9517(82)90075-6</u>.

(3) Barteau, M. A. Is it time to stop searching for better catalysts for oxidative coupling of methane? *Journal of Catalysis* **2022**, *408*, 173-178. DOI:

https://doi.org/10.1016/j.jcat.2022.03.006.

(4) Ramaiyan, K. P.; Denoyer, L. H.; Benavidez, A.; Garzon, F. H. Selective electrochemical oxidative coupling of methane mediated by Sr2Fe1.5Mo0.5O6- δ and its chemical stability. *Communications Chemistry* **2021**, *4* (1), 139. DOI: 10.1038/s42004-021-00568-1.

(5) Zavyalova, U.; Holena, M.; Schlögl, R.; Baerns, M. Statistical Analysis of Past Catalytic Data on Oxidative Methane Coupling for New Insights into the Composition of High-Performance Catalysts. *ChemCatChem* **2011**, *3* (12), 1935-1947. DOI:

https://doi.org/10.1002/cctc.201100186.

(6) Alvarado Flores, J. J.; Ávalos Rodríguez, M. L.; Andrade Espinosa, G.; Alcaraz Vera, J. V. Advances in the development of titanates for anodes in SOFC. *International Journal of Hydrogen Energy* **2019**, *44* (24), 12529-12542. DOI:

https://doi.org/10.1016/j.ijhydene.2018.05.171.

(7) Bai, L.; Polo-Garzon, F.; Bao, Z.; Luo, S.; Moskowitz, B. M.; Tian, H.; Wu, Z. Impact of Surface Composition of SrTiO3 Catalysts for Oxidative Coupling of Methane. *ChemCatChem* 2019, *11*(8), 2107-2117, <u>https://doi.org/10.1002/cctc.201900159</u>. DOI:

https://doi.org/10.1002/cctc.201900159 (acccessed 2023/02/06).

(8) Zhang, S.-L.; Wang, H.; Lu, M. Y.; Zhang, A.-P.; Mogni, L. V.; Liu, Q.; Li, C.-X.; Li, C.-J.; Barnett, S. A. Cobalt-substituted SrTi0.3Fe0.7O3–δ: a stable high-performance oxygen electrode material for intermediate-temperature solid oxide electrochemical cells. *Energy & Environmental Science* 2018, *11* (7), 1870-1879, 10.1039/C8EE00449H. DOI: 10.1039/C8EE00449H.

(9) Rothschild, A.; Menesklou, W.; Tuller, H. L.; Ivers-Tiffée, E. Electronic Structure, Defect Chemistry, and Transport Properties of SrTi1-xFexO3-y Solid Solutions. *Chemistry of Materials* **2006**, *18* (16), 3651-3659. DOI: 10.1021/cm052803x. (10) Marina, O. A.; Canfield, N. L.; Stevenson, J. W. Thermal, electrical, and electrocatalytical properties of lanthanum-doped strontium titanate. *Solid State Ionics* **2002**, *149* (1), 21-28. DOI: <u>https://doi.org/10.1016/S0167-2738(02)00140-6</u>.

(11) Wang, J.; Yang, J.; Opitz, A. K.; Bowman, W.; Bliem, R.; Dimitrakopoulos, G.; Nenning, A.; Waluyo, I.; Hunt, A.; Gallet, J.-J.; et al. Tuning Point Defects by Elastic Strain Modulates Nanoparticle Exsolution on Perovskite Oxides. *Chemistry of Materials* **2021**, *33* (13), 5021-5034. DOI: 10.1021/acs.chemmater.1c00821.

(12) Tsvetkov, N.; Lu, Q.; Sun, L.; Crumlin, E. J.; Yildiz, B. Improved chemical and electrochemical stability of perovskite oxides with less reducible cations at the surface. *Nature Materials* **2016**, *15* (9), 1010-1016. DOI: 10.1038/nmat4659.

(13) Kodama, S.; Kikuchi, R.; Fujiwara, N.; Tada, S.; Kobayashi, Y.; Oyama, S. T. Oxidative Coupling of Methane in Solid Oxide Electrolysis Cell. *ECS Transactions* **2019**, *91* (1), 2697. DOI: 10.1149/09101.2697ecst.