



# Solid oxide electrolysis: Concluding remarks

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Renewable energy resources such as solar energy, wind energy, hydropower or geothermal energy have attracted significant attention in recent years. Renewable energy sources have to match supply with demand, therefore it is essential that energy storage devices (e.g., secondary batteries) are developed. However, secondary batteries are accompanied with critical problems such as high cost for the limited energy storage capacity and loss of charge over time. Energy storage in the form of chemical species, such as H<sub>2</sub> or CO<sub>2</sub>, have no constraints on energy storage capacity and will also be essential. When plentiful renewable energy exists, for example, it could be used to convert H<sub>2</sub>O into hydrogen via water electrolysis. Also, renewable energy resources could be used to reduce CO<sub>2</sub> into CO and recycle CO<sub>2</sub> and H<sub>2</sub>O into sustainable hydrocarbon fuels in solid oxide electrolysis (SOE).

## Introduction

High temperature solid oxide electrolysis (HT-SOE) is a promising candidate technology that could play a key role in the transition to sustainable energy. The high temperature operation (heat energy) maximizes its efficiency and high reaction rate, offering thermodynamic and kinetic advantages. However, there are still some drawbacks when the cell is operated in SOE mode. One of the most important issues in SOE mode is the oxygen electrode degradation, which is attributed to the formation of a secondary phase and delamination of the oxygen electrode. For realization of a commercial SOE technology, it is necessary to develop robust and efficient electrodes and study more systematic fundamental physicochemical and electrochemical properties including surface chemistry and defect chemical behavior.

Recently, Graves *et al.* reported that operating a SOC in a reversible cycling mode between electrolysis and fuel-cell modes, similar to a rechargeable battery, inhibits the microstructural deterioration and long-term degradation compared with constant electrolysis operation.<sup>1</sup> SOCs (solid oxide cells) can both store renewable electricity as fuels (electrolysis mode) and convert fuels to electricity

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(fuel cell mode). Incorporating SOECs and SOFCs into a single device that can work reversibly with high and comparable efficiency will provide significant overall cost benefits.

This discussion held in York brought together researchers from a wide range of disciplines, *i.e.*, fundamental electrochemistry, materials development, system, durability and oxygen electrodes, within the excellent traditional *Faraday Discussions* format, to discuss advances in areas relevant to the main theme of the meeting.

## Fundamental electrochemistry

Kee *et al.* (DOI: 10.1039/c5fd00012b) developed new experimental and modeling approaches to establish thermodynamics ( $\Delta H^\circ$  and  $\Delta S^\circ$ ) and transport properties (diffusion and surface kinetics) in a multiple charged defect conducting (MCDC) ceramic, yttrium-doped barium zirconate (BZY10). Because widely-practiced models, such as ambipolar diffusion theory, are not directly applicable to MCDCs, a more complex formulation based on the Nernst–Planck–Poisson was developed. The measured enthalpy and entropy changes and kinetics representing the incorporation of  $H_2$ ,  $O_2$ , and  $H_2O$  may give insight into efficient hydrogen production using SOEs based on proton conducting materials.

Graves *et al.* (DOI: 10.1039/c5fd00048c) discussed both model and porous electrodes to obtain useful information for a more realistic technological electrode in SOCs. The conventional fuel-electrode material, a composite of nickel and yttria/scandia stabilized zirconia (Ni–SZ), is known to be more active for  $H_2/H_2O$  than for  $CO/CO_2$  reactions. The ratio of electrode polarization resistance in  $CO/CO_2$  vs.  $H_2/H_2O$  decreases from 33 to 2. Besides showing higher activity for  $H_2/H_2O$  reactions than  $CO/CO_2$  reactions, Ni–SZ is more active for oxidation than reduction. Graves *et al.* found the opposite behavior in both cases for CGO/STN model electrodes, thus reflecting the unprecedented observation of a higher electrocatalytic activity of CGO nanoparticles for  $CO/CO_2$  than for  $H_2/H_2O$  reactions in the absence of a gas diffusion limitation.

In order to better understand the nature of the electrocatalytic activities observed for different electrode materials and geometries, which vary considerably for these reactions, they measured and compared AC impedance and DC current-overpotential for Ni–SZ, 3 phase boundary (3PB), and CGO nanoparticles on a porous mixed ionic conductor such as  $Sr_{0.94}Ti_{0.9}Nb_{0.1}O_3$  (STN) backbones, 2 phase boundary (2PB). The enhanced surface reduction of nano CGO on STN results in a higher ratio of  $CO/CO_2$  vs.  $H_2/H_2O$  and more activity on  $CO_2$  reduction than  $H_2O$  reduction *via* increased surface concentrations of oxygen vacancies and polarons ( $Ce^{3+}$ ). They also pointed out that a Pt current collector may selectively enhance the activity of the  $H_2/H_2O$  reaction.

Cumming *et al.* (DOI: 10.1039/c5fd00030k) at the University of Sheffield developed and designed an analytical tool to fully understand and characterize co-electrolysis of carbon dioxide and steam to produce syngas, *in situ* monitoring of the reactions, products, and SOC. They emphasized the importance of *in situ* or *operando* analysis of fuel cells and electrolyzers. This *in situ* spectroscopy could provide invaluable information about the surfaces and species involved in the overall macroscopic reaction, along with information on the complex interplay of reactions occurring during co-electrolysis. Diffuse reflectance infrared Fourier

transform spectroscopy (DRIFT) is ideal for the detection of CO and CO<sub>2</sub> species, and has previously not been used for this purpose. The designed rig has been used for symmetric cell testing at temperatures from 450 to 600 °C. In contrast with *ex situ* experiments, *in situ* DRIFT gives significant changes related to a combination of CO oxidation, the water gas shift reaction, and carbonate formation and decomposition processes, with the dominant process being both potential and temperature dependent. Further development is expected to allow the use of asymmetric cells in the presence of different atmospheres.

What is a real surface? Is the surface oxygen exchange rate at the true outer surface linked to bulk ion diffusivity in mixed conducting materials, *e.g.* Ruddlesden–Popper (RP) phases? McIntosh *et al.* (DOI: 10.1039/c5fd00014a) tried to determine a correlation between bulk ion mobility and the surface exchange rate between materials. They measured each rate with separate techniques, *in situ* neutron diffraction and pulsed isotopic surface exchange, respectively, for three RP phases, such as the general form  $A_{n-1}A'_2B_nO_{3n+1}$  ( $n = 1, 2$  and  $3$ ). The surface exchange rates vary by more than one order of magnitude with high anion mobility in the bulk of an oxygen vacancy-rich  $n = 2$  RP material, correlating with rapid oxygen exchange. Even though it was concluded that surface oxygen incorporation is not rate limiting in these materials, the challenge of determining the true outer surface oxygen exchange rate experimentally remains.

Proton conducting solid oxide fuel cells (PCFCs) have attracted significant attention in recent years due to their advantages, such as higher ionic conductivity of electrolytes compared to oxide ion conductors, no dilution of the fuel with water vapor, faster start-up, and less degradation.<sup>2</sup> The reduction of the PCFC operating temperature, however, causes a drop of the electrocatalytic activity, which occurs especially in the cathode process.<sup>3</sup> In this meeting, Merkle *et al.* (DOI: 10.1039/c5fd00013k) presented thermogravimetric properties which changed to conditions of lower and higher  $p_{O_2}$  and rationalized the observed changes in the defect chemical behavior. By considering the defect relationship between three mobile carriers (*i.e.*  $V_{O}^{\bullet}$ ,  $OH_{O}^{\bullet}$ , and holes), the concentrations of oxygen vacancies, protons, and holes can be calculated numerically as a function of  $K_{O}p_{O_2}^{1/2}$  and  $K_{W}p_{H_2O}^{1/2}$ . From the calculated results, one can recognize that the proton uptake of materials having high redox-activity is mainly compensated by hole consumption (*i.e.* hydrogenation), while the proton uptake of electrolyte materials is mainly compensated by  $V_{O}^{\bullet}$  (*i.e.* hydration). In addition, the thermogravimetric investigation of  $Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$  (BSFZ) under various  $p_{O_2}$  atmospheres shows that BSFZ incorporates a non-negligible amount of protons and the mode of proton incorporation changes from hydration (at low  $p_{O_2}$ ) to hydrogenation (at high  $p_{O_2}$ ), indicating that the presence of oxygen vacancies is not necessarily required for the proton uptake.

The surface and near-surface chemical composition of electroceramic materials often shows significant deviations from that of the bulk. The oxygen transport properties and their relationship with the surface chemistry in cation-ordered  $GdBaCo_2O_{5+\delta}$  (GBCO) perovskite were investigated by Téllez *et al.* (DOI: 10.1039/c5fd00027k) using Low Energy Ion Scattering (LEIS) spectroscopy and <sup>18</sup>O tracer exchange coupled with Secondary Ion mass Spectrometry (SIMS). The LEIS showed that the surface and near-surface composition is very dynamic, and significant compositional changes can occur at relatively low temperatures and short time periods with accompanying structural rearrangements. In particular,

GBCO exhibited rapid segregation of the divalent Ba cation to the surface to form a BaO terminated layer, suggesting that a multiphase material is formed at the near-surface. Despite the different surface compositions and the extension of the Ba segregation profile, the surface exchange coefficients ( $k^*$ ) appeared to be less sensitive to the surface composition than anticipated, even though the cation segregation led to a significantly different surface in terms of the Ba surface coverage. From these results, it appears that the near-surface disorder introduced by the cation segregation might have a more powerful influence on the observed surface exchange kinetics than the surface termination.

A reversible SOFC (RSOFC) with mixed ion-electron conducting (MIEC) with a simplified cell design and lower manufacturing costs was studied with  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  (LSFCr-3) by Birss *et al.* (DOI: 10.1039/c5fd00029g). RSOFCs can run in the electrolysis mode (SOEC) to store energy by converting  $\text{H}_2\text{O}$  to  $\text{H}_2$  and  $\text{O}_2$ , or co-electrolyze  $\text{CO}_2$  and  $\text{H}_2\text{O}$  to syngas and  $\text{O}_2$ . The fuel cell mode (SOFC) can convert  $\text{H}_2$  or syngas, and oxygen, to electricity and heat when electricity is needed with available excess electricity. Their careful electrochemical studies with 3 electrode half-cell impedance allowed them to isolate the reactions occurring in the fuel cell and electrolysis modes and determine the catalytic activity of the material towards each reaction separately. Interestingly, LSFCr-3 is a better catalyst for oxygen evolution and  $\text{CO}_2$  reduction than for oxygen reduction or CO oxidation, indicating overall better performance in the electrolysis *vs.* fuel cell mode.

## Material development

Various types of materials such as simple perovskite oxides and layered perovskite oxides have been investigated as electrodes for solid oxide electrolysis cells. Among them, pure oxide fuel electrodes have been attracting much interest because commercial cermet fuel electrodes require permanent circulation of a reducing gas (*e.g.*  $\text{H}_2$  or CO, called a safe gas) to avoid oxidation of the metallic phase. Torrell *et al.* investigated steam/ $\text{CO}_2$  co-electrolysis with a symmetrical solid oxide electrolysis cell consisting of reversible  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$  (LSCM) electrodes and an ytterbium scandium stabilized zirconia ( $(\text{ZrO}_2)_{0.9}$ - $(\text{Yb}_2\text{O}_3)_{0.06}(\text{Sc}_2\text{O}_3)_{0.04}$ , YbScSZ) electrolyte (DOI: 10.1039/c5fd00018a). They demonstrated that no safe gas is required when using symmetrical full ceramic SOEC cells and ratios of  $\text{H}_2$  : CO of about 2 were obtained, meeting the requirement for the synthesis of standard hydrocarbon fuels or alcohols. However, significant degradation was also observed under galvanostatic operation conditions, caused by delamination of the oxygen-electrolyte interface. This may be associated with an increase of the internal oxygen pressure close to the surface of the oxygen electrode.

A new layered perovskite oxide transformed from a simple perovskite under a reducing atmosphere was introduced earlier this year.<sup>4</sup> The layered perovskite ( $\text{PrBaMn}_2\text{O}_{5+\delta}$ ) oxide exhibits high electrical conductivity, excellent redox tolerance and coking tolerance. It is a promising cathode material for  $\text{CO}_2$  electrolysis (DOI: 10.1039/c5fd00025d). By an *in situ* high temperature X-ray diffraction study, a reversible phase change between  $\text{PrBaMn}_2\text{O}_{5+\delta}$  (layered perovskite) and  $\text{PrBaMn}_2\text{O}_{6-\delta}$  (simple perovskite) during redox cycles was confirmed. An

electrolysis cell using a layered perovskite oxide ( $\text{PrBaMn}_2\text{O}_{5+\delta}$ ) exhibited a fairly high performance.

The remarkable electrolysis cell performance originates from the highly mixed ionic and electronic conductivity of the pure oxide fuel electrode. Mixed ionic and electronic conducting (MIEC) materials have been used not only as electrodes but also as membranes for air separation and for production of syngas (a mixture of CO and  $\text{H}_2$ ). Yu *et al.* investigated oxygen permeation fluxes in mixed ionic and electronic conducting (MIEC) membranes based on composites of 40 vol%  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$  (LSCr) and 60 vol% yttria stabilized zirconia (YSZ). Oxygen fluxes in MIEC membranes consisting of LSCr and YSZ are often limited by surface reactions and can be improved by modifying the surface morphology with inflation of the MIEC (DOI: 10.1039/c5fd00007f).

Tsvetkov *et al.* (DOI: 10.1039/c5fd00023h) emphasized that surface modification can improve the surface oxygen kinetics and stability through suppression of Sr segregation and phase separation of dopant cations from the A-site, driven by elastic and electrostatic energy minimization and kinetic demixing. Careful surface modification was performed by adding the optimum amount of Ti (10%) into  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  (LSC) by dipping the latter into a chemical bath of  $\text{TiO}_4$  solution. Interestingly, the oxygen exchange kinetics on LSC-T cathodes was found to be up to 8 times higher than on bare LSC cathodes and their stability was retained. This kind of simple surface modification can open up a new route for stabilization and better electrochemical performance for perovskite oxide electrodes for high temperature electro- and thermo-chemical applications.

Composites consisting of a perovskite-based electronic or mixed conductor with a fluorite-structured ionic conductor are often used as electrodes in solid oxide electrochemical energy conversion devices. For fabricating the composite electrode, the composite materials are usually sintered at high temperature. However, after sintering the materials, inter-reactions between the two phases, or inter-diffusion of cations or impurities between the two phases, are often observed. Durce *et al.* studied the  $^{18}\text{O}$  exchange properties and surface composition of a composite consisting of  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (CGO) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) in a 50 : 50 ratio by a high resolution time of flight-secondary ion mass spectrometry (ToF-SIMS) analysis and LEIS spectroscopy (DOI: 10.1039/c5fd00028a). High resolution ToF-SIMS mapping revealed that the  $^{18}\text{O}$  fraction of the composite is much higher than expected from the diffusivity ( $D^*$ ) and surface exchange coefficient ( $k^*$ ) values for the single-phase parent material. By a surface compositional analysis with ToF-SIMS and LEIS spectroscopy, they confirmed that the surfaces of the CGO grains in the composite do not show impurities, which typically segregate into the surface in single-phase CGO. In order to explain this phenomenon, they considered three mechanisms: (1) catalytic spill-over; (2) activation of the CGO surface by incorporation of transition metals; and (3) cleaning of the CGO surface by the dissolution of impurities into the LSCF. Due to the absence of evidence to support mechanism (2), they concluded the apparent enhanced surface exchange for CGO in these composites may be related with mechanisms (1) and (3), or a combination of the two.

Novel materials compatible with YSZ should be developed for better performance as the oxygen electrode of RSOFCS at temperatures below 800 °C for the purpose of using metallic interconnects, enhancing stability, and reducing maintenance expenses. Ni *et al.* (DOI: 10.1039/c5fd00026b) introduced

$\text{CaMn}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$  (CMN) with Nb doping as a novel oxygen electrode through an investigation of crystal structure, electrochemical characterization, physical/chemical property variations, and the difference in electrochemical performance of the oxygen electrode from  $\text{CaMnO}_{3-\delta}$  (CM) and  $\text{CaMn}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$  (CMN) materials under SOE and SOFC operating conditions. The crystal structure of CM and CMN was determined to be an orthorhombic structure. The  $\delta$  values of CM and CMN were analyzed by TGA and changed to 0.099 and 0.025 at 900 °C in air, respectively. The changes of oxygen content caused by the valence variation of the transition metal were anticipated to be beneficial to the electrochemical performance of the oxygen electrode.<sup>5</sup> At 700 °C, CM, as a cathode for SOFCs, achieved a polarization resistance of less than  $0.1 \Omega \text{ cm}^2$ , while CMN showed superior performance ( $R_p < 0.1 \Omega \text{ cm}^2$  at 0.4 V bias) as an anode for SOECs. A possible candidate material with a Nb content of less than 10 mol% doping on the Mn site would lead to better oxygen electrode performance in both SOFC and SOE modes.

## System studies

For commercialization of a solid oxide electrolysis cell, in addition to fundamental issues, systemic issues should also be discussed. The study of high temperature (HT) steam/ $\text{CO}_2$  co-electrolysis is much more complicated than that of HT steam or  $\text{CO}_2$  electrolysis because (1) apart from electrochemical reactions, the chemical reverse water–gas shift reaction (RWGS) also plays an important part in the formation of CO, (2) the equilibrium of the RWGS is highly sensitive to the outlet gas temperature from the electrolysis cell, and (3) the performance and syngas composition change significantly with the microstructure of the SOECs and the operating conditions.<sup>6–8</sup> Wang *et al.* investigated reaction characteristics and the outlet syngas composition of high temperature (HT) steam/ $\text{CO}_2$  coelectrolysis under different operating conditions with a single cell ( $5 \times 5 \text{ cm}^2$ ) at 800 °C (DOI: 10.1039/c5fd00017c). Through a comparison of the area specific resistance (ASR) under different fuel conditions, it was confirmed that the RWGS more significantly contributes to the formation of CO than the electrochemical reduction reaction. The outlet syngas composition from HT steam/ $\text{CO}_2$  coelectrolysis is very sensitive to the operating conditions.

Previously, performance maps based on closed form isothermal parametric models for both hydrogen and natural gas fuelled SOFC stacks have been demonstrated.<sup>9</sup> By applying this approach, Milobar *et al.* determined the power and the efficiency of a solid oxide electrolysis stack over a wide range of operating conditions (DOI: 10.1039/c5fd00015g). The determined values were then confirmed with estimated costs of principal components and sized for specific system design criteria to obtain a cost/performance model. The model was used to map the performance of a stack and the cost elements for a given set of performance parameters across the operating space in voltage and specific steam flow rate. Component sizing and cost estimates were used to predict the total system capital cost. A cost analysis framework is a useful tool to reveal opportunities for system optimization and cost minimization.

Tao *et al.* introduced a new application of solid oxide electrolysis cell. They directly synthesized ammonia from wet air at 400 °C using a solid oxide electrolysis cell consisting of a  $\text{Sm}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$  electrode and a  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  and ternary carbonate mixture ( $\text{Li, Na, K})_2\text{CO}_3$  (32.1 wt%  $\text{Li}_2\text{CO}_3$ ;

34.5 wt%  $\text{K}_2\text{CO}_3$ ; 33.4 wt%  $\text{Na}_2\text{CO}_3$ ) electrolyte (DOI: 10.1039/c5fd00033e). The ammonia formation rate was more than two orders of magnitude higher than that when synthesized from  $\text{N}_2$  and  $\text{H}_2\text{O}$  at 600 °C.<sup>10</sup> The electrode material was also inexpensive compared to commercial catalysts for ammonia synthesis from air and water.

## Understanding durability

Recently, a higher-efficiency storage method utilizing a reversible solid oxide cell (ReSOC) has been proposed.<sup>11</sup> One key question regarding ReSOCs is their long-term durability. Hughes *et al.* (DOI: 10.1039/c5fd00020c) presented the degradation of solid oxide cell  $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}-\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{2-\gamma}$  (LSM-YSZ) composite oxygen electrodes during reversing current operation. Degradation was characterized by impedance spectroscopy in symmetrical LSM-YSZ/YSZ/LSM-YSZ cells tested at 800 °C in air with a symmetric current cycle with a period of 12 hours. No change in cell resistance could be detected in 1000-h tests with a sensitivity of ~1% per kh, at a current density of 0.5  $\text{A cm}^{-2}$  corresponding to an overpotential of 0.18 V, while higher current/overpotential values at a current density of 0.6  $\text{A cm}^{-2}$  (0.33 V overpotential) led to faster degradation. As the authors indicated, the polarization degradation, mainly observed at higher current density, is associated with the resistance of YSZ grain boundaries within the electrode from an increase in LSM particle size and a decrease in the amount of YSZ and LSM at the electrode/electrolyte interface.

Similar to the problems facing solid oxide fuel cell (SOFC) technology, a notable issue is poisoning of the air electrode by impurities such as Cr released from metallic interconnects or balance-of-plant components.<sup>12</sup> Egger *et al.* (DOI: 10.1039/c5fd00021a) investigated  $\text{La}_2\text{NiO}_{4+\delta}$  (LNO) as a potential anode material for high temperature solid oxide electrolyzer cells (SOECs). Long-term durability was tested at 800 °C for 140 days (~3300 hours), applying current densities up to  $-410 \text{ mA cm}^{-2}$  under a pure  $\text{Ar/O}_2$  atmosphere as well as in the presence of chromium and humidity. After 46 days (1100 h) in a pure 20%  $\text{O}_2/\text{Ar}$  atmosphere, Cr was added under dry conditions and after another 41 days (1000 h) 30% relative humidity was introduced into the gas stream. A total increase in the anode ASR of 350% from 0.22 to 1.0  $\Omega \text{ cm}^2$  was observed. A clear effect of Cr in dry/humid conditions on the degradation behavior unfortunately could not be revealed from cell measurements. Cr was not detected by EDX in the SOEC anode after long-term operation, indicating that Cr-poisoning may have an imperceptible influence on LNO electrodes under anodic polarization. Poor electrode-electrolyte contact or partial delamination is probably responsible for the observed performance degradation of the LNO anode.

Generally, the state-of-the-art commercial solid oxide cell (SOC) uses Ni-YSZ as the fuel electrode material. Operation of a Ni-YSZ electrode supported Solid Oxide Cell (SOC) was investigated by Ebbesen *et al.* (DOI: 10.1039/c5fd00032g), who showed the operation of a SOC in both fuel cell mode (FC-mode) and electrolysis cell mode (EC-mode) in mixtures of  $\text{H}_2\text{O}/\text{H}_2$ ,  $\text{CO}_2/\text{CO}$ , and  $\text{H}_2\text{O}/\text{H}_2\text{O}/\text{CO}_2/\text{CO}$  at 750 °C, 800 °C, and 850 °C. The observed area specific resistance (ASR) values in both  $\text{H}_2\text{O}/\text{H}_2$  and  $\text{CO}_2/\text{CO}$  mixtures are lower for oxidation than for reduction. Further, the ASR (both  $\text{ASR}_{\text{fuel cell}}$  and  $\text{ASR}_{\text{electrolysis}}$ ) values were higher for  $\text{CO}_2/\text{CO}$  mixtures compared to the ASR values for  $\text{H}_2\text{O}/\text{H}_2$  mixtures due to lower activity for

CO oxidation/CO<sub>2</sub> reduction compared to H<sub>2</sub> oxidation/H<sub>2</sub>O reduction. The slower kinetics for reduction was found to be partly related to the polarization heating and the entropy change. Due to the exothermic reaction in FC-mode and the endothermic reaction in EC-mode, both the ohmic resistance and the electrochemical electrode resistance are higher in EC-mode as compared to FC-mode. The effect of changing the porosity was also discussed by Ebbesen *et al.* during the meeting. The polarization in EC-mode at decreasing porosity increased, indicating that diffusion limitations cannot be neglected for support structures with porosity below 30% (with a support thickness of 300 μm). These diffusion limitations through the support and active electrode structure create an increased reducing atmosphere at the interface, which may be related to the degradation of the cells.

Fabrication routes for new SOEC mesoporous nanocomposite materials as electrodes were presented by Torrell *et al.* (DOI: 10.1039/c5fd00035a). Ceramic-metal (cermet) mesoporous composites of Ni-CGO obtained after reduction of mesoporous NiO impregnated with CGO were employed as a fuel electrode while samarium strontium cobaltite (Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-δ</sub>/SSC) impregnated scaffolds of mesoporous samarium doped ceria (Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub>/SDC) were used as the oxygen electrode. The maximum value of injected current density at 1.7 V was 330 mA cm<sup>-2</sup> with significant ohmic resistance at a temperature of 850 °C. This is likely to be due to insufficient adhesion of the electrode to the electrolyte caused by the high thermal stability of the mesoporous materials. Therefore, optimization of the electrode attachment temperatures should be pursued in future studies, especially when high thermal stability materials such as this are used.

## Oxygen electrodes

Chen *et al.* (DOI: 10.1039/c5fd00010f) investigated the activity and stability of La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM) oxygen electrodes for the first time under solid oxide electrolysis cell (SOEC) operating conditions at 800 °C in the presence of an Fe–Cr interconnect. Cr deposition occurs in the LSM electrode bulk and in particular on the YSZ electrolyte surface and on the LSM electrode inner surface close to the electrode/electrolyte interface. The results showed the formation of Cr, CrO<sub>0.87</sub>, Cr<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>5</sub>, and SrCrO<sub>4</sub> on the YSZ electrolyte surface, within the contact rings and on the LSM inner surface. The observation of SrCrO<sub>4</sub> formation on the LSM electrode under SOEC operating conditions is attributable to anodic polarization promoting Sr segregation. The segregated Sr species could be highly mobile and readily spread to the YSZ electrolyte surface because of the high activity of gaseous Cr species with segregated Sr species. Chen *et al.* also presented clear evidence that the delamination or failure of LSM oxygen electrodes is primarily due to the disintegration or breaking of LSM particles attached to the YSZ electrolyte surface. The excess segregation of Sr could also result in partial decomposition of LSM, and this appears to be supported by the shift of Mn2p<sub>3/2</sub> to a lower binding energy (BE) of 639.5 eV under the rib of the interconnect.<sup>13</sup> This may indicate partial decomposition of the LSM perovskite phase on the YSZ surface under the rib of the interconnect.

Nano-sized composite electrodes were fabricated by infiltration technology and subsequently sintered at relatively low temperatures (700–900 °C),<sup>14</sup> which effectively hinders the formation of insulating phases. Nano-sized SSC–YSZ



oxygen electrodes prepared by an infiltration process for SOFCs/SOECs were investigated by Fan *et al.* (DOI: 10.1039/c5fd00022j). The electrochemical performance of the cell was determined under both fuel cell and steam electrolysis modes using polarization curves and electrochemical impedance spectroscopy (EIS). The current densities of a Ni-YSZ/YSZ/SSC-YSZ cell at an electrolysis voltage of 1.3 V are 0.91 mA cm<sup>-2</sup>, 0.70 mA cm<sup>-2</sup>, 0.45 mA cm<sup>-2</sup>, and 0.27 mA cm<sup>-2</sup> at 800 °C, 750 °C, 700 °C, and 650 °C, respectively. The Ni-YSZ/YSZ/SSC-YSZ cell showed gradual degradation during electrolysis over 100 h in 50% H<sub>2</sub>O, 25% H<sub>2</sub>, and 25% N<sub>2</sub> due to delamination of the oxygen electrode from the electrolyte and agglomeration of SSC particles. Moreover, segregation of cobalt-enriched particles (particularly cobalt oxides) at the interface is likely related to cell degradation under the steam electrolysis mode.

The performance of a molten carbonate electrolysis cell (MCEC) is, to a great extent, determined by the anode, *i.e.* the oxygen production reaction at the porous NiO electrode.<sup>15</sup> The stationary polarization curves for the NiO electrode under varying gas compositions and temperatures were analyzed by Hu *et al.* (DOI: 10.1039/c5fd00011d). The activation energy of the NiO porous electrode for oxygen production decreased between 278 and 211 kJ mol<sup>-1</sup> when increasing the O<sub>2</sub> concentration from 1.5 to 30%. In contrast, the value increased from 124 to 229 kJ mol<sup>-1</sup> with increasing CO<sub>2</sub> content from 2.5 to 40%. Gas compositions of low O<sub>2</sub> partial pressure, *e.g.* 1.5–10% O<sub>2</sub>, exhibit much larger activation energies than those with low CO<sub>2</sub> partial pressure, which means that oxygen appears to have a stronger effect on charge-transfer limitation. This indicates that the NiO electrode for oxygen production is generally under a charge-transfer limitation, except at very low CO<sub>2</sub> partial pressure where it is under mixed control. As the activation energy is evident in determining the rate-determining process,<sup>16</sup> it is probable that the NiO electrode is under mixed control at quite low CO<sub>2</sub> concentrations. Also, the reaction  $\text{CO}_3^{2-} \rightleftharpoons \text{O}^{2-} + \text{CO}_2$  is considered to play an important role at low CO<sub>2</sub> partial pressure in oxygen production in MCEC mode.

## Final comments

This meeting beginning with the possibility that a SOE would be the best energy conversion and storage technology to realize sustainable energy was held in the quaint city of York. The SOEC is only a reverse reaction of a SOFC, but there are some difficulties to solve as it has a more complicated electrochemical reaction and system than those of the SOFC, which is the common view of the participants. The newly developed technologies and prospects were discussed throughout this meeting, especially including fundamental electrochemistry, the overall results of new materials, systems, and durability in the traditional manner of *Faraday Discussions*. Some researchers introduced various types of materials such as simple perovskite oxides and layered perovskite oxides as electrodes with high electrolysis performance for solid oxide electrolysis cells. In particular, Professor Mogensen asked 'the most frequent questions' to participants and his enthusiasm made the meeting more effective. I believe these enthusiastic efforts and vision will realize the industrialization of SOE on a worldwide scale in the near future. I would like to close my comments with an expression of my heartfelt gratitude to the organizing committee members, including John T. S. Irvine, Raymond J. Gorte, Tatsumi Ishihara, Mogens Mogensen, Truls Norby and John Varcoe.

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