Evaluation of novel ZnO–Ag cathode for CO₂ electroreduction in solid oxide electrolyser

Saheli Biswas² · Aniruddha P. Kulkarni² · Aaron Seeber¹ · Mark Greaves¹ · Sarbjit Giddey¹ · Sankar Bhattacharya²

Received: 16 October 2021 / Revised: 10 December 2021 / Accepted: 13 December 2021 / Published online: 21 January 2022
© The Author(s) 2021

Abstract

CO₂ and steam/CO₂ electroreduction to CO and methane in solid oxide electrolytic cells (SOEC) has gained major attention in the past few years. This work evaluates, for the very first time, the performance of two different ZnO–Ag cathodes: one where ZnO nanopowder was mixed with Ag powder for preparing the cathode ink (ZnO_{mix}–Ag cathode) and the other one where Ag cathode was infiltrated with a zinc nitrate solution (ZnO_{inf}–Ag cathode). ZnO_{mix}–Ag cathode had a better distribution of ZnO particles throughout the cathode, resulting in almost double CO generation while electrolysing both dry CO₂ and H₂/CO₂ (4:1 v/v). A maximum overall CO₂ conversion of 48% (in H₂/CO₂) at 1.7 V and 700 °C clearly indicated that as low as 5 wt% zinc loading is capable of CO₂ electroreduction. It was further revealed that for ZnO_{inf}–Ag cathode, most of CO generation took place through RWGS reaction, but for ZnO_{mix}–Ag cathode, it was the synergistic effect of both RWGS reaction and CO₂ electrolysis. Although ZnO_{inf}–Ag cathode produced trace amount of methane at higher voltages, with ZnO_{mix}–Ag cathode, there was absolutely no methane. This seems to be due to strong electronic interaction between Zn and Ag that might have suppressed the catalytic activity of the cathode towards methanation.

Keywords ZnO–Ag cathode · CO₂ electroreduction · ZnO distribution · Zn–Ag intermetallic phase

Introduction

Issues related to the over-exploitation of fossil fuels coupled with the alarming emission of greenhouse gases have made a compelling case for atmospheric CO₂ recycling via conversion to valuable fuels and chemicals. Many such approaches are being explored that allow effective valorisation of CO₂, one of the most promising ones being electrolytic routes where CO₂ captured from air undergoes electrochemical reduction along with water into chemical feedstocks and fuels [1–4]. If the fuel produced is methane, it can be stored and transported or directly injected into the existing natural gas grids. Otherwise, if it is a smaller molecule like CO, it can be further utilised as a raw material for downstream processing to synthesise other valuable chemicals.

CO₂ is a highly stable molecule with a C=O bond dissociation energy of 750 kJ/mol [5], resulting in a high activation barrier for its electrochemical conversion [6]. Moreover, electrochemical CO₂ reduction in an aqueous environment at lower temperatures is a complex process that involves multi-electron/proton transfer processes coupled with numerous possible reaction intermediates and products [7–9]. CO₂ electroreduction in solid oxide electrolytic cells (SOEC) involves a less complicated reaction pathway and has been a topic of great interest in the past many years [3, 4, 10, 11]. The cathode electrode where electroreduction of CO₂ occurs is key component that needs further development and optimisation to achieve target selectivity and conversion rates using minimal energy.

The state-of-the-art cathode material for SOEC is a composite of Ni and 8 mol% yttria stabilized zirconia (8YSZ) that has limited activity towards CO₂ electrolysis. Aaberg et al. [12] performed both steam and CO₂ electrolysis with Ni–YSZ cathode and reported polarization resistance 2–5 times higher for CO/CO₂ than for H₂/H₂O. Green et al. [13] also observed significant degradation of the cell performance while electrolysing a CO₂/CO mixture using Ni–YSZ cathode. They further reported that

✉ Aniruddha P. Kulkarni
aniruddha.kulkarni@monash.edu

¹ CSIRO Energy, Private Bag 10, Victoria,
Clayton South 3169, Australia

² Department of Chemical and Biological Engineering,
Monash University, 3800 Victoria, Australia

in a CO rich environment Ni catalyses Boudouard reaction, leading to carbon deposition and cathode passivation. Similar observations have been reported by Sukeshini et al. [14] who studied the oxidation of H_2 , CO and CO/ H_2 mixtures using Ni electrodes on YSZ electrolyte. They observed that under no-load conditions, the area specific resistance in CO/Ar (1:3) was almost double compared to H_2 /Ar (1:3). Additionally, it is well documented in the literature that Ni causes several issues [15–17], such as agglomeration, particle coarsening, migration away from the electrode–electrolyte interface increasing overall cell resistance and oxidation to catalytically inactive NiO phase. In response to the above challenges pertaining to Ni-YSZ, alternative ceramic materials like fluorites and perovskites are being widely investigated for CO_2 electrolysis and steam/ CO_2 co-electrolysis [3, 18, 19].

ZnO is a semiconductor material that has not been evaluated so far as a cathode material for CO_2 electroreduction to CO or methane. It has been widely investigated as a support material for H_2 production via steam reforming of ethanol and methanol [20, 21], and as a photocatalyst for splitting water to H_2 [22–24]. However, only a handful of literature is available where ZnO has been used as a catalyst for methanation or reverse water gas shift (RWGS) reaction [25–29]. Lee et al. [26] investigated Fe-Zn bimetallic catalyst for synthetic natural gas production from syngas hydrogenation, and reported a very high CO conversion of ~98.2% with methane selectivity of 25% at 300 °C and 10 bars. Recently, Le et al. [27] studied CO_2 /CO methanation on Zn promoted Ni/ Al_2O_3 catalyst and reported conversion of ~100% at 400 °C and 1 bar but low methane selectivity. Contrarily, Dias et al. [28] reported CO_2 conversion of 50% with methane selectivity of 80% with Zn promoted Ni/ SiO_2 . Based on the above reports, we have investigated the effect of presence of ZnO in the cathode on CO_2 conversion while electrolysing dry CO_2 as well as an H_2 / CO_2 (4:1 v/v) mixture in a tubular solid oxide electrolyser. ZnO is an n-type semiconductor and its electrical conductivity depends on the number of O_2 vacancies present in the lattice [30, 31]. Its conductivity increases in a reducing atmosphere and can be further increased by doping with an electron donor metal oxide like alumina (Al_2O_3). However, to study the fundamental behaviour of ZnO for such applications, we restricted our experiments to undoped ZnO. Ag is used as additional conducting phase. We studied the electroreduction using reliable tubular cells with two different approaches for fabrication of ZnO-Ag cathode [32, 33]. In the first approach, Ag cathode was infiltrated with a $Zn(NO_3)_2$ solution to achieve a nominal zinc loading of 5 wt%. In the second approach, ZnO nanopowder was mechanically mixed with Ag powder in appropriate ratio to obtain 5 wt% zinc and then used this to prepare the cathode ink. Subsequently, the performance of both these cathodes in dry CO_2 and H_2 / CO_2 atmospheres

was evaluated between 500 and 700 °C for the very first time to the authors' knowledge.

Materials and methods

Cell fabrication

Tubular SOECs were fabricated with ZnO–Ag cathode, 8YSZ electrolyte and a composite of Ag and gadolinia doped ceria ($Gd_{0.1}Ce_{0.9}O_{2.8}$) as anode. Ag–GDC had previously depicted good mechanical and chemical stability in an oxidizing environment and appreciable catalytic activity towards oxygen evolution reaction [32, 33], so was chosen as the anode. Two different techniques were used to introduce ZnO into our cathode.

The tubular cells tested here were electrolyte supported, so the first step was to fabricate the tube. Eight molecular percent yttria-stabilized zirconia (8YSZ) powder (Tosoh Corporation Japan) was subjected to isostatic pressing at 170 MPa and sintered in air [34] in binder burn-off furnace. The sintering profile consisted of a heating phase to 1500 °C at 1.6 °C/min followed by a dwell phase at 1500 °C for 4 h and then a cooling phase to 900 °C at 1.6 °C/min and to 25 °C at 3 °C/min. The nominal cell thickness was 0.045 cm. Next step involved brush-coating the tube with the cathode ink over a length of 12 cm to get electrode area of 33 cm².

For the ZnO infiltrated Ag cathode (ZnO_{inf} -Ag), a silver ink was first prepared by mixing Ag powder (Alfa Aesar, 3-micron ASP) and ink vehicle (Fuel Cell Materials Inc.) and ball milling the same for 2 h. Then the ink was brush-coated on the inside walls of the tube followed by sintering in a binder burn-off furnace at 825 °C for 2 h, using heating and cooling rates of 180 °C/h. Following this, the anode ink was prepared by ball milling 35 wt% $GdCeO_{2.8}$ (Fuel Cell Materials Inc.) and 65 wt% Ag powder with ink vehicle. The as-prepared ink (Ag-GDC) was brush-coated on the outside of the tube cell and sintered the same binder burn-off furnace at 825 °C for 2 h, using heating and cooling rates of 180 °C/h. Each electrode was ~40 µm thick with an effective cell area of 33 cm². In the next step (infiltration), 50 ml of 1 M zinc nitrate solution in Millipore water was prepared using $Zn(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich). The as-prepared tube cell was tightly fixed to a tripod and the bottom of the tube was masked using a rubber cork. Twenty-five millilitre of the zinc nitrate solution was poured inside the tube and allowed to stand for 3 h. Next, the solution was drained by removing the cork and the tube was sintered at 825 °C for 2 h, using ramp rates of 180 °C/h. The same infiltration step was repeated once again so as to achieve ~5 wt% nominal Zn loading. One millimetre thick Ag wires were wound on both the electrodes for current collection. A schematic of the major steps is shown in Fig. 1a.

Fig. 1 A schematic of the major steps involved in tube cell fabrication with ZnO_{inf} -Ag cathode a and ZnO_{mix} -Ag cathode b

For fabricating the ZnO mixed Ag cathode (ZnO_{mix} -Ag) ink was prepared by ball milling 5 wt% ZnO nanopowder (Sigma Aldrich) and 95 wt% Ag powder with ink vehicle (Fig. 1b). The ink was then brush-coated on the inner walls of a freshly pressed tube cell over a length of 12 cm and sintered at 825 °C at a ramp rate of 180 °C/h. Subsequently, the Ag-GDC anode ink was coated on the outside of the tube and sintered at 825 °C using the same heating profile. Each electrode was $\sim 40 \mu\text{m}$ thick with an effective cell area of 33 cm^2 . One millimetre thick Ag wires were wound on both the electrodes for current collection.

Electrochemical testing

The tubular cell was placed inside a horizontal tubular furnace with high precision temperature controller and heated to 500 °C in 99.9% pure N_2 . Subsequently, dry CO_2 was fed to the cathode at a constant feed rate (50 mL/min). The voltage–current (V – I) characteristics and impedance spectrum at open-circuit voltage (OCV) were recorded with an Ivium potentiostat. The gas mixture exiting the cathode was collected in gasbags for 40 min, and its composition was analysed using gas chromatography (GC) (Agilent Micro GC). Next, the cell was loaded at 1.5 V and the impedance spectrum was recorded (once the cell had stabilized after almost 30 min) along with the collection of the gas mixture evolving at the cathode followed by GC analyses. The same sequence was maintained to obtain data at 600 and

700 °C, as well. All these tests at the three different temperatures were performed using two separate 8YSZ electrolyte-supported tube cells, one with ZnO_{inf} -Ag cathode and the other one with ZnO_{mix} -Ag cathode. Next, the same tests were repeated with the same tube cells but under an H_2/CO_2 (4:1 v/v) atmosphere and under applied potentials ranging from 1.3 to 1.9 V. It is to be noted that all V – I curves were scanned at 5 mV/s and electrochemical impedance spectra were recorded between 10 kHz and 0.1 Hz at an amplitude of 70 mV.

Physical characterisation

Powder X-ray diffraction (XRD) of the fresh and tested cathode was carried out in a Bruker D8 Advance A25 X-ray Diffractometer operating under $\text{CuK}\alpha$ radiation (40 kV, 40 mA) equipped with a Lynx Eye XE-T detector. The sample was scanned over the 2θ range 5 to 130° with a step size of 0.02° and a count time of 1.6 s per step and was spun at 15 RPM during data collection. Analyses were performed on the collected XRD data using the Bruker XRD search match program EVATM5. Crystalline phases were identified using the ICDD-JCPDS powder diffraction database. Rietveld analyses were performed on the data using the Bruker TOPASTM V6 program to determine phase wt% and lattice parameter values. Background signal was described using a combination of Chebyshev polynomial linear interpolation function and $1/x$ function. A Merlin scanning electron microscope

Fig. 2 Impedance spectra recorded with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode while electrolysing dry CO_2 at 500, 600 and 700 °C at OCV **a** and at 1.5 V **b** along with the corresponding voltage-current curves **c**. Inset in **b** shows an exploded view of the impedance spectra at 600 and 700 °C. Voltage-current curves recorded with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode while electrolysing dry CO_2 at 500, 600 and 700 °C **d** along with impedance spectra at those temperatures at OCV and 1.5 V **e**

coupled with energy-dispersive X-ray (SEM–EDX) was used for imaging the microstructure and elemental distribution of fresh and tested cathodes.

Table 1 R_{ohm} and R_{pol} for $\text{ZnO}_{\text{inf}}\text{-Ag}$ and $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathodes under dry CO_2 atmosphere at OCV and 1.5 V between 500 and 700 °C with corresponding CO_2 and CO percentages

Cathode	Temperature (°C)	Applied voltage (V)	R_{ohm} ($\Omega\text{-cm}^2$)	R_{pol} ($\Omega\text{-cm}^2$)	CO_2 (%)	CO (%)	CO_2 conversion (%)
$\text{ZnO}_{\text{inf}}\text{-Ag}$	500	OCV	44.47	63.53	100	0.00	0.00
		1.5	44.12	4653.88	100	0.00	0.00
	600	OCV	9.16	13.34	99.93	0.07	0.07
		1.5	8.98	491.02	99.67	0.33	0.33
	700	OCV	4.09	8.41	99.01	0.99	0.99
		1.5	3.97	326.03	98.29	1.71	1.71
$\text{ZnO}_{\text{mix}}\text{-Ag}$	500	OCV	40.26	77.74	100	0.00	0.00
		1.5	40.01	5.88	100	0.00	0.00
	600	OCV	9.53	36.21	99.89	0.11	0.11
		1.5	9.03	8.89	99.20	0.80	0.80
	700	OCV	3.90	14.10	98.30	1.70	1.70
		1.5	3.87	4.14	97.09	3.91	3.91

Results and discussion

Performance of two different ZnO -based cathodes towards CO_2 electrolysis

Two tube cells, $\text{ZnO}_{\text{inf}}\text{-Ag|8YSZ|AG-GDC}$ and $\text{ZnO}_{\text{inf}}\text{-Ag|8YSZ|AG-GDC}$, were tested at 500, 600 and 700 °C in dry CO_2 atmosphere. Figure 2a, b depict the impedance spectra recorded with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode at OCV and at 1.5 V, respectively. As expected, at both OCV and 1.5 V, ohmic resistance (R_{ohm}) and polarization resistance (R_{pol}) decreased with temperature, indicating higher ionic conductivity and improved cell kinetics at elevated temperature. However, at any particular temperature, R_{pol} increased dramatically from OCV to 1.5 V (Table 1). The trend depicted by the V – I curves (Fig. 2c) mirrored what had been observed with bare Ag electrodes in our previous work [32]. The kink in the V – I curves represents very high impedance up to ~1.4 V resulting in almost no increase in current density with increasing potential. Beyond 1.4 V, there was an increase in current density, albeit minimal that indicated the onset of CO_2 electrolysis. This agrees with the impedance trends where a substantial increase in R_{pol} from OCV to 1.5 V has been observed (Table 1). With $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, current density at any particular voltage was almost 20 times higher (Fig. 2d) than $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode. Additionally, for the $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, current density increased monotonically with temperature, whereas $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode showed no significant increase in current density until above 1.4 V at all temperatures. Also, unlike $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode R_{pol} decreased upon increasing the applied potential from OCV to 1.5 V (Fig. 2e). In fact, at 1.5 V, R_{pol} values at all three temperatures were smaller than the corresponding R_{ohm} values, indicating that the process was mostly ohmic controlled, whereas, for $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, the process was polarization controlled

at both OCV and 1.5 V (Table 1). This can be better understood by a careful qualitative inspection of the impedance spectra recorded with both the cathodes.

The OCV impedance spectra of $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode (Fig. 2a) at 500 °C consisted of a single huge arc (spanning over high and mid frequencies) followed by a small low frequency tail. According to previous reports [13, 35], the huge arc comprises activation polarization (R_{act}) of the electrodes and concentration polarization (R_{con}) [13, 36, 37], whereas the tail resembling Warburg impedance could be due to diffusion resistance and resistance to $\text{CO}_2\text{-CO}$ surface exchange reaction. With further increase in temperature, the single arc got depressed and the tail became more prominent, gradually taking the shape of a second arc. It is possible that at a lower temperature of 500 °C, R_{act} and R_{con} were the major contributors to R_{pol} , whereas with increase in temperature diffusion and surface-reduction of CO_2 became the rate-limiting steps. At 1.5 V, the impedance spectra consisted of a single huge arc that could be decoupled into a high frequency arc followed by a Warburg type arc. Contrarily, the impedance spectra of $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode (Fig. 2e) at OCV consisted of a single arc that shrunk in size at an applied potential of 1.5 V. This was observed at all three temperatures. Such single huge arcs usually encompass contributions from several processes. Thus, an exact interpretation of the contribution from each process involves deconvolution of the spectra using circuit modelling or using Kramer-Kronig's technique, which may not be accurate for a tubular cell with area as large as 33 cm^2 .

A comparison of the R_{ohm} and R_{pol} values obtained with the two different cathodes (Table 1) revealed that both exhibited very similar R_{ohm} values at any particular temperature confirming reproducible cell fabrication. However, R_{pol} values widely varied between $\text{ZnO}_{\text{mix}}\text{-Ag}$ and $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathodes. At OCV, R_{pol} was slightly higher for $\text{ZnO}_{\text{mix}}\text{-Ag}$, and this was consistently observed at all three test temperatures. Contrarily, at 1.5 V, R_{pol} with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode was orders of magnitude less than that for $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode. Since the anode was the same (Ag-GDC) for both the tube cells, we surmise that the disparity in the R_{pol} values can be attributed to the cathode. It is also to be noted that both the cathodes essentially had the same composition (~95% Ag and rest ZnO), the only difference being the synthesis process. This clearly reflects the direct effect of cathode synthesis technique on the overall cell performance, which is further corroborated by an analysis of the gas chromatography data.

Both the cathodes exhibited no CO_2 conversion at 500 °C at OCV as well as at 1.5 V. However, at 600 and 700 °C at OCV, CO_2 conversion with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode was respectively 0.07 and 0.99% that increased by ~1.2 times with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode. Since electrolysis could not have occurred under no-load conditions, such CO_2 conversion at OCV (albeit minimal) can be attributed to its surface

reduction to CO in presence of ZnO. A possible explanation behind the superior catalytic behaviour of $\text{ZnO}_{\text{mix}}\text{-Ag}$ could be a more uniform distribution of ZnO throughout the cathode as was found through SEM imaging coupled with SEM-EDX mapping (discussed in detail in the “SEM characterization of two different ZnO-based cathodes”). Upon increasing the applied voltage to 1.5 V, CO_2 conversion with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode increased to 0.33 and 1.71% at 600 and 700 °C, respectively. With $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, the corresponding CO_2 conversion values were 0.80 and 3.91%. Thus, it is clear that as low as 5 wt% nominal Zn loading can lead to CO_2 electrolysis where $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode proved to be more effective, indicating the importance of synthesis technique towards overall cell performance.

Performance of two different ZnO-based cathodes towards H_2/CO_2 electrolysis

The same two tube cells were tested at 500, 600 and 700 °C in H_2/CO_2 (4:1 v/v) atmosphere. The $V\text{-}I$ curves with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode (Fig. 3a) showed trends similar to what had been observed with bare Ag electrodes in our previous work [32]. Maximum current density was ~12 mAcm^{-2} at 700 °C and 2 V. Trends depicted by the impedance spectra (Fig. 3b, c and d) were very similar to what had been observed in dry CO_2 atmosphere discussed in the “Performance of two different ZnO-based cathodes towards CO_2 electrolysis”. R_{ohm} was almost constant under all applied potentials at a particular temperature (Table 2), but R_{pol} first increased and then gradually decreased. For instance, at 500 °C, R_{pol} increased from 78.88 $\Omega\text{-cm}^2$ at OCV to 2359.75 $\Omega\text{-cm}^2$ at 1.5 V and then started reducing. At 600 and 700 °C, R_{pol} increased from OCV to 1.3 V and then started decreasing. Similar observations have been reported in our previous work where we studied Fe infiltrated Ag electrodes for H_2/CO_2 (4:1 v/v) electrolysis [33].

Contrarily, with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, the R_{pol} at all test temperatures dropped systematically from OCV till the maximum applied potential of 1.9 V (Fig. 4a, b and c). Compared to $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, $\text{ZnO}_{\text{mix}}\text{-Ag}$ showed remarkably more uniform distribution of ZnO particles throughout the cathode as confirmed through SEM imaging (discussed in detail in the “SEM characterization of two different ZnO-based cathodes”). In presence of H_2 and upon the application of voltage, oxygen vacancies are created in ZnO lattice that act as oxide ion conductors. Thus, more uniform ZnO distribution may imply an even distribution of oxygen vacancies across the cathode that can effectively expand the electron-ion-gas triple phase boundary (TPB), which plays a major role in electrochemical reactions [38]. Thus, at any particular temperature and applied potential, R_{pol} recorded with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode was almost two orders of magnitude lesser than what had been obtained with $\text{ZnO}_{\text{inf}}\text{-Ag}$

Fig. 3 Voltage-current curves recorded with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode while electrolysing a mixture of H_2/CO_2 (4:1 v/v) at 500, 600 and 700 °C **a** along with the impedance spectra at OCV and different loaded conditions at 500 °C **b**, 600 °C **c** and 700 °C **d**

cathode in spite of R_{ohm} being similar for both. The resulting current density (Fig. 4d) was also almost two orders of magnitude higher than $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode.

In fact, at all applied voltages above 1.5 V, R_{pol} values for $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode were smaller than the corresponding R_{ohm} values (Table 2), indicating that the process was mostly ohmic controlled. In contrast, R_{pol} values for $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode were remarkably higher than the corresponding R_{ohm} values irrespective of voltage (Table 2). So, the process was clearly polarization controlled.

Table 2 shows $\text{CO}\%$, $\text{CH}_4\%$ and $\text{CO}_2\%$ obtained from GC analysis of the gases leaving the cathode under specific

conditions of temperature and applied voltage. Both the cathodes generated CO at OCV and the amount increased monotonically with temperature. H_2/CO_2 electrolysis is accompanied by many reactions such as reverse water gas shift (RWGS) producing CO and steam (Eq. 1), CO_2 electrolysis producing CO (Eq. 1), methanation (Eq. 3) and methane dissociation (Eq. 4).

Since electrolysis is not feasible at OCV, the CO must have been generated from RWGS reaction as well as surface reduction of CO_2 to CO (in case of $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode) as had been envisaged during dry CO_2 electrolysis (discussed in the previous “Performance of two different ZnO-based cathodes towards CO_2 electrolysis”). As is clearly visible, $\text{CO}\%$ with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode was almost two to four times higher than what had been generated with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode. Similar trends are reflected in the CO_2 conversion as well (Fig. 5a). As can be seen from Fig. 5a, b, for $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode CO_2 and H_2 conversions were very similar, thus suggesting CO generation through mostly RWGS reaction as is easily perceptible from the reaction stoichiometry (Eq. 1). Contrarily, with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, CO_2 conversion was almost double the H_2 conversion, indicating CO production via both RWGS reaction and CO_2 electrolysis. Now, the question arises why the conversion through RWGS reaction gradually increased with applied voltage for $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode as is evident from the increasing trend of the CO percentage (Table 1). As already mentioned in our previous work [32, 33], the steam generated through RWGS reaction compete with CO_2 for electrolysis, and on cathode materials that are not electrocatalytically active towards CO_2 electroreduction, the steam gets electrolysed since it is kinetically more favourable. With increase in applied voltage, more steam is electrolysed, thus further promoting the RWGS reaction resulting in more H_2 and CO_2 conversion.

Interestingly, neither $\text{ZnO}_{\text{inf}}\text{-Ag}$ nor $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode showed any evidence of CO_2 conversion at 1.5 V and 500 °C under dry CO_2 atmosphere (Table 1), whereas, under the same conditions of temperature and voltage in H_2/CO_2 atmosphere, $\text{ZnO}_{\text{inf}}\text{-Ag}$ and $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathodes exhibited 1.93 and 5.62% CO_2 conversion, respectively. While for $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, most of the conversion took place through RWGS reaction, for $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, it was the synergistic effect of both RWGS reaction and

Table 2 R_{ohm} and R_{pol} for ZnO_{inf} -Ag and ZnO_{mix} -Ag cathodes under H_2/CO_2 (4:1 v/v) atmosphere at different loaded conditions at 500–700 °C with corresponding CH_4 , CO_2 and CO percentages

Cathode	Temperature (°C)	Applied voltage (V)	Current (mAcm ⁻²)	R_{ohm} (Ω-cm ²)	R_{pol} (Ω-cm ²)	CO ₂ (%)	CH ₄ (%)	CO (%)
ZnO_{inf}-Ag	500	OCV	0.00	42.56	78.88	19.82	0.000	0.21
		1.3	0.21	42.30	1559.70	19.75	0.000	0.23
		1.5	0.46	42.25	2359.75	19.61	0.000	0.29
		1.7	0.57	42.17	2059.83	19.45	0.000	0.43
		1.9	0.74	42.09	359.91	19.29	0.004	0.65
	600	OCV	0.00	9.98	14.30	19.13	0.000	0.91
		1.3	0.31	9.89	1241.11	19.01	0.000	0.96
		1.5	1.01	9.67	851.33	18.99	0.000	1.01
		1.7	1.61	9.54	251.46	18.87	0.005	1.18
		1.8	2.35	9.43	391.57	18.48	0.010	1.54
	700	OCV	0.00	4.39	8.74	18.35	0.000	1.72
		1.3	0.44	4.32	185.68	18.08	0.000	1.83
		1.5	1.91	4.23	170.77	17.78	0.006	2.14
		1.7	3.56	4.20	138.80	17.26	0.015	2.67
		1.9	6.65	4.15	60.85	16.69	0.031	3.40
ZnO_{mix}-Ag	500	OCV	0.00	40.77	41.31	19.57	0.000	0.43
		1.3	20.62	40.36	40.81	19.28	0.000	0.72
		1.5	23.99	40.08	14.78	18.88	0.000	1.12
		1.7	27.66	39.86	6.69	17.88	0.000	2.12
		1.9	31.69	39.59	5.40	16.82	0.000	3.18
	600	OCV	0.00	10.24	42.75	18.02	0.000	1.98
		1.3	42.06	9.58	38.41	17.53	0.000	2.47
		1.5	50.06	9.24	10.67	16.75	0.000	3.25
		1.7	58.30	9.15	5.74	15.41	0.000	4.59
		1.9	63.00	9.01	2.64	13.65	0.000	6.35
	700	OCV	0.00	3.94	11.06	16.45	0.000	3.55
		1.3	89.93	3.85	1.15	14.99	0.000	5.01
		1.5	108.11	3.80	0.83	12.78	0.000	7.22
		1.7	122.90	3.78	0.28	10.48	0.000	9.52

CO₂ electrolysis. Similarly, at 600 and 700 °C, CO₂ conversion with ZnO_{mix} -Ag cathode was much higher in H_2/CO_2 compared to dry CO₂ under the same applied potential. The higher CO₂ electrolysis efficacy of the same material (ZnO_{mix} -Ag) in H_2/CO_2 atmosphere can be attributed to H_2 creating more oxygen vacancies in ZnO, thus enhancing the surface adsorption of CO₂, which is a vital step for CO₂ electrolysis.

Another interesting observation was that with ZnO_{inf} -Ag cathode, trace amounts of methane were obtained (Table 2) but with ZnO_{mix} -Ag cathode, there was no methane at all. Previously, Wang et al. [30] studied Ni/ZnO and Ni/Al₂O₃ catalysts for CO₂ methanation and reported that while Ni/Al₂O₃ gave CO conversion of ~89%, Ni/ZnO gave only 7% at 350 °C. They concluded from electron paramagnetic resonance spectroscopy (EPR) and X-ray photoelectron

Spectroscopy (XPS) studies that singly ionized oxygen vacancies in ZnO lattices gave electrons to Ni atoms, thus creating a strong electronic metal-support interaction that drastically changed the electronic properties of Ni. As a result, CO molecules were linearly adsorbed and not bridge-adsorbed (as was seen from in situ DRIFTS spectra), thus leading to the suppression of methanation activity. Similar observation has been very recently reported by Chen et al. [39] who studied CO₂ reduction to methanol on Au/ZnO catalysts. Based on these reports, we surmise that in our case, possibly a strong electronic interaction might have been established between ZnO and Ag, resulting in the suppression of methanation. The effect was more pronounced for ZnO_{mix} -Ag cathode where ZnO particles were uniformly distributed throughout the cathode surface. Thus, ZnO_{mix} -Ag cathode generated no methane at all. SEM-EDX

Fig. 4 Impedance spectra recorded with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode while electrolyzing a mixture of H_2/CO_2 (4:1 v/v) under OCV and different loaded conditions at 500 °C **a**, 600 °C **b** and 700 °C **c** along with the corresponding voltage-current curves **d**

imaging of fresh and tested cathodes also supports this conjecture as discussed later in the “SEM characterization of two different ZnO -based cathodes”.

Fig. 5 CO_2 **a** and H_2 **b** conversions obtained with $\text{ZnO}_{\text{inf}}\text{-Ag}$ and $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathodes under H_2/CO_2 atmosphere at different loaded conditions between 500 and 700 °C

SEM characterization of two different ZnO -based cathodes

The fresh $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode exhibited a porous structure with sporadic clusters of ZnO nanoparticles (Fig. 6a).

This indicates that the infiltration method had resulted in non-uniform distribution of ZnO . When using infiltration techniques for metal introduction inside a support material, different parameters come into play that include precursor composition, solvent used, calcination temperature and ramp rates. Using a different metal precursor like zinc acetate or a different solvent like ethanol can influence the ZnO distribution. Reducing the calcination temperature from 825 to around 500 °C (usually preferred temperature

Fig. 6 SEM image of fresh $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode **a** showing ZnO clusters. Magnified views **b** and **c** of one such cluster circled in yellow in **a** along with SEM-EDX map **d** and individual elemental maps showing Zn **e**, Ag **f** and O **g**. SEM image of tested $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode **h** showing ZnO clusters, magnified view **i** of one such cluster circled in yellow in **h** along with SEM-EDX map **j** and individual elemental maps showing Ag **k**, Zn **l** and O **m**

for heterogeneous catalyst preparation using wet impregnation method) or manoeuvring the heating and cooling rates could also potentially improve the ZnO dispersion. It is well known that increasing the calcination temperature leads to grain growth and increase in metal particle size that can sometimes lead to clustering or agglomeration. Similarly, the heating rate and the chemical form of the metal precursor or intermediates formed during calcination (e.g. nitrate versus oxide) influence the concentrations of H_2O , NH_3 and NO_x released and may also affect the severity of local exotherms caused by decomposition or reduction reactions. A detailed analysis of the effect of these parameters on ZnO dispersion would be an interesting study to be conducted in future. Figure 6b shows an exploded view of one such ZnO cluster. It is comprised of a dense network of ZnO nanoparticles and resembled a structure similar to self-assembled ZnO nanorods [40, 41], often referred to as ZnO flowers. Individual ZnO particles showed uniformity of shape with sizes ranging from 100 to 200 nm (Fig. 6c). SEM–EDX (Fig. 6d, e, f and g) maps further confirm the non-uniform distribution of ZnO nanoparticles. The tested ZnO_{inf} –Ag cathode showed morphology very similar to the fresh one (Fig. 6h). There were sporadic ZnO clusters formed by a dense 3D network of self-assembled ZnO nanoparticles (Fig. 6i). Individual particles appeared to have fused together into slightly larger sizes; however, exact interpretation requires higher resolution TEM images, which is out of the scope of this work. EDX maps confirmed the non-uniform distribution of ZnO clusters (Fig. 6j, k, l and m).

The fresh ZnO_{mix} –Ag cathode depicted a completely different morphology as seen from Fig. 7a, b. ZnO distribution was more uniform as confirmed through SEM–EDX mapping (Fig. 7c, d, e and f) as well. ZnO particles were present all over the electrode surface; however, mostly concentrating near and within the pores formed between adjacent Ag particles (Fig. 7g). This is clearly perceptible from the EDX map captured at a higher magnification (Fig. 7h, i, j and k). Individual ZnO particles were characterized by heterogeneity in terms of shape and size. Sizes mostly varied between 100 and 500 nm.

The tested ZnO_{mix} –Ag electrode showed morphology very dissimilar to the fresh one (Fig. 8). Sporadic clusters of ZnO particles are observed as shown in Fig. 8a, b. Surprisingly, no ZnO particles were visible on the larger Ag particles unlike in case of fresh cathode. Either they might have percolated deep inside the pores of the Ag network or they might have disintegrated into smaller nanoparticles that require higher magnification imaging. Figure 8c and d show exploded views of the ZnO cluster shown in Fig. 8a. Individual particles were packed into a 3D network and varied in size from 200 to 600 nm. Figure 8e, f present exploded views of the ZnO cluster shown in Fig. 8b. Here the individual ZnO particles were slightly larger (500 to 1000 nm)

Fig. 7 SEM image of fresh ZnO_{mix} –Ag cathode **a** and its magnified view **b** along with SEM–EDX map **c** showing uniform ZnO clusters. Individual elemental maps showing Ag **d**, Zn **e** and O **f**. Magnified view of the cathode at 10,000X **g** along with SEM–EDX map **h** and individual elemental maps showing Zn **i**, Ag **j** and O **k**

and formed a 2D network. Why the two clusters depicted such different morphologies is a subject of further investigation through TEM imaging. Another interesting observation was the difference in the surface topography of the Ag particles of fresh and used ZnO –Ag electrodes. While the Ag particles of the fresh electrode showed a smooth topography (Fig. 8g), the ones on the used electrode had a rough and rugged topography (Fig. 8h). While the EDX map of fresh electrode showed evidence of ZnO near the edges of individual Ag particles (Fig. 7h), the EDX map of used electrode showed the existence of ZnO all over the Ag surface (Fig. 8i and m). A possibility is the migration of ZnO particles under the impact of applied potential, and formation of an intermetallic phase between Zn and Ag under the influence of strong electronic metal-support interaction (EMSI) as reported elsewhere [30, 39]. (Fig. 8j, k and l show the individual maps of silver, zinc and oxygen on the fresh cathode, whereas Fig. 8n, o and p show the same for the used

Fig. 8 SEM image of tested $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode at two different spots **a** and **b** showing ZnO clusters. The ZnO cluster in **a** at 5000X **c** and 10,000X **d** magnifications. The ZnO cluster in **b** at 5000X **e** and 10,000X **f** magnifications. SEM image of larger Ag particles decorated with ZnO nanoparticles for fresh $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode at 10,000X **g** and image of Ag particle for tested $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode at 10,000X **h**. SEM-EDX of ZnO cluster **i** along with individual elemental maps showing Ag **j**, Zn **k** and O_2 **l**. SEM-EDX of another ZnO cluster **m** along with individual elemental maps showing Ag **n**, Zn **o** and O_2 **p**

cathode). In case of $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, ZnO particles were present as self-assembled clusters that are usually highly stable, and thus might have prevented any particle migration or electronic interaction with Ag. Another factor could be ZnO particle size as well. While studying the activity of Au/ZnO catalyst towards CO_2 reduction to methanol, Chen et al. [39] reported that increasing ZnO particle size increased the electronic interaction between Au and ZnO, thus affecting overall methanol selectivity and yield. In our study, ZnO particles on $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode varied in size from 100 to 500 nm as opposed to a size range of 100 to 200 nm for $\text{ZnO}_{\text{inf}}\text{-Ag}$. The larger particle size could be another reason behind the interaction between Zn and Ag envisaged with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode. However, accurate interpretation requires electron paramagnetic resonance (EPR) analysis, which is a matter to investigate in the future.

XRD characterization of two different ZnO-based cathodes

Figure 9 shows the X-ray diffractograms of fresh and tested cathodes. In both the fresh and tested $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode (Fig. 9a), the major phases detected were hexagonal ZnO

and cubic Ag along with cubic $\text{Y}_{0.06}\text{Zr}_{0.94}\text{O}_{1.97}$ coming from the electrolyte. The ZnO phase was not clearly discernible because the particles were nano-sized. Sharper reflections of ZnO can be obtained using high-resolution synchrotron-based powder diffraction, which is out of the scope of this work. Similarly, fresh and tested $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode depicted hexagonal ZnO, cubic Ag and cubic $\text{Y}_{0.06}\text{Zr}_{0.94}\text{O}_{1.97}$ as the major phases. Compared to fresh $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, the ZnO peaks were more prominent for fresh $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode possibly because of their slightly larger size (100 to 500 nm) as had been seen from SEM images as well. This can be better understood from the exploded diffractograms shown in Fig. 9b. Fresh $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode showed sharp reflections from ZnO at 31.7° , 34.5° and 36.4° , whereas fresh $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode exhibited stunted reflections. For tested $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, ZnO peaks became shorter and broader compared to fresh cathode, indicating particle size reduction, and for tested $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode they became very noisy and almost indiscernible. Rietveld refinement showed that the ZnO lattice parameter was similar (~ 5.20 nm) for all the four cathodes. However, corresponding ZnO crystallite sizes were notably dissimilar as calculated from the Scherrer equation. In fresh $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, ZnO crystallite

Fig. 9 X-ray diffractogram of fresh and tested $\text{ZnO}_{\text{mix}}\text{-Ag}$ and $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathodes **a** with a magnified view of the same between 29 and 37° Bragg's angle **b**

size was 59 nm that reduced to 20 nm for tested cathode. Contrarily, for fresh $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, ZnO crystallite size was 110 nm (almost double that of fresh $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode) that dropped to 30 nm for tested cathode. This observation matches well with our findings from SEM imaging and SEM-EDX mapping and confirms that application of voltage in a reducing atmosphere (H_2/CO_2) led to ZnO particle size reduction and possibly some sort of electronic interaction between Ag and Zn.

The Ag peaks also broadened for tested cathodes, indicating size reduction. For $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, Ag crystallite size reduced from 225 to 46 nm. For $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, Ag crystallite size reduced from ~1000 to 170 nm. Similarly, the $\text{Y}_{0.06}\text{Zr}_{0.94}\text{O}_{1.97}$ peaks also broadened and became stunted for tested cathodes indicating crystallite size reduction. The $\text{Y}_{0.06}\text{Zr}_{0.94}\text{O}_{1.97}$ reflections from both $\text{ZnO}_{\text{mix}}\text{-Ag}$ and $\text{ZnO}_{\text{inf}}\text{-Ag}$ tested cathodes exhibited slight peak shift to lower angle, which denotes lattice expansion. One possibility could be dissolution of Zn^{2+} ion into the YSZ lattice, but nothing like this has been reported in the literature. A more realistic possibility is the chemical reduction of yttrium and

zirconium after being continuously exposed to a reducing environment during H_2/CO_2 electrolysis. Similar conclusions have been made by Pomfret et al. [42] from X-ray photoelectron spectroscopic (XPS) studies on fresh YSZ and a sample exposed to H_2 environment at 1000 °C. Nonetheless, an exact interpretation requires further streamlined analysis using XPS and X-ray nanotomography.

Based on the above observations from X-ray diffractograms and SEM analyses, it is further proved that the electrode synthesis process affects the crystallite size of the particles, their distribution and the overall surface topography.

Conclusion

A novel ZnO-based cathode has been tested, for the very first time, for studying CO_2 reduction in a single temperature SOEC by electrolysis CO_2 alone and a mixture of H_2/CO_2 (4:1 v/v) at 500, 600 and 700 °C. Two different synthesis methods have been evaluated, one where the Ag cathode was infiltrated with a zinc nitrate solution to introduce ZnO particles ($\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode), and the other method where ZnO nanopowder was mixed with Ag powder to prepare the cathode ink ($\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode). SEM imaging coupled with EDX mapping revealed that ZnO distribution was more uniform in $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, whereas in $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode the ZnO particles formed sporadic clusters of self-assembled structures. As a result, oxygen vacancy distribution (upon exposure to H_2/CO_2) was more uniform on $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode. This was manifested by a monotonically decreasing R_{pol} with voltage for the $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode. Contrarily, with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, R_{pol} first increased dramatically from OCV to a certain applied voltage and then decreased. Consequently, CO production at any temperature and voltage with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode was almost thrice that with $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode. It is worth mentioning that with CO_2 alone as well, the conversions of CO_2 were more than twice at 600 °C and 700 °C for $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode compared to $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode. The CO_2 and H_2 conversion trends revealed that for $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode, most of CO generation took place through RWGS reaction, but for $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, it was the synergistic effect of both RWGS reaction and CO_2 electrolysis. Maximum CO_2 and H_2 conversion were ~48 and 22%, respectively, at an applied potential of 1.7 V at 700 °C. This clearly shows that even as low as 5 wt% nominal zinc loading is capable of CO_2 conversion to CO in a reducing environment, i.e. in the presence of H_2 . It was also observed that $\text{ZnO}_{\text{inf}}\text{-Ag}$ cathode produced trace amount of methane at higher voltages, but with $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode, there was absolutely no methane. A possibility is strong electronic interaction between ZnO and Ag that might have suppressed the catalytic activity of the cathode towards methanation. The effect was more

pronounced for $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode where the ZnO particles were uniformly dispersed throughout the surface, resulting in a stronger interaction. SEM–EDX mapping showed evidence of Ag–Zn intermetallic state formation on the tested $\text{ZnO}_{\text{mix}}\text{-Ag}$ cathode but not on the $\text{ZnO}_{\text{inf}}\text{-Ag}$. Nonetheless, there is scope for further investigation through electron paramagnetic resonance analysis and in operando Fourier transform infrared spectroscopy.

Funding Open Access funding enabled and organized by CAUL and its Member Institutions. This research is funded by the Research and Development Program (Renewable Hydrogen for Export) of the Australian Renewable Energy Agency (ARENA). Additional support has been received from CSIRO Hydrogen Energy Systems Future Science Platform and CSIRO Research Office. The funders were not involved in the experimental design or the collection, analysis and interpretation of data, or writing of the manuscript or the decision to submit it for publication.

Declarations

Conflict of interest The authors declare no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Wang Y, Diaz DFR, Chen KS, Wang Z, Adroher XC (2020) Materials, technological status, and fundamentals of PEM fuel cells—a review. *Mater Today* 32:178–203
- Centi G, Quadrelli EA, Perathoner S (2013) Catalysis for CO 2 conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries. *Energy Environ Sci* 6(6):1711–1731
- Kaur G, Kulkarni AP, Giddey S (2018) CO2 reduction in a solid oxide electrolysis cell with a ceramic composite cathode: effect of load and thermal cycling. *Int J Hydrogen Energy* 43(48):21769–21776
- Kaur G, Kulkarni AP, Giddey S, Badwal SP (2018) Ceramic composite cathodes for CO2 conversion to CO in solid oxide electrolysis cells. *Appl Energy* 221:131–138
- Li K, Peng B, Peng T (2016) Recent advances in heterogeneous photocatalytic CO2 conversion to solar fuels. *ACS Catal* 6(11):7485–7527
- Verma S, Kim B, Jhong HRM, Ma S, Kenis PJ (2016) A gross-margin model for defining technoeconomic benchmarks in the electroreduction of CO2. *Chemsuschem* 9(15):1972–1979
- Kortlever R, Shen J, Schouten KJP, Calle-Vallejo F, Koper MT (2015) Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide. *J Phys Chem Lett* 6(20):4073–4082
- Gattrell M, Gupta N, Co A (2006) A review of the aqueous electrochemical reduction of CO2 to hydrocarbons at copper. *J Electroanal Chem* 594(1):1–19
- Durst J, Siebel A, Simon C, Hasché F, Herranz J, Gasteiger H (2014) New insights into the electrochemical hydrogen oxidation and evolution reaction mechanism. *Energy Environ Sci* 7(7):2255–2260
- Küngas R, Blennow P, Heiredal-Clausen T, Holt T, Rass-Hansen J, Primdahl S, Hansen JB (2017) eCOs—a commercial CO2 electrolysis system developed by Haldor Topsoe. *ECS Trans* 78(1):2879
- Song Y, Zhang X, Xie K, Wang G, Bao X (2019) High-temperature CO2 electrolysis in solid oxide electrolysis cells: developments, challenges, and prospects. *Adv Mater* 31(50):1902033
- Costamagna P, Costa P, Antonucci V (1998) Micro-modelling of solid oxide fuel cell electrodes. *Electrochim Acta* 43(3–4):375–394
- Green RD, Liu C-C, Adler SB (2008) Carbon dioxide reduction on gadolinia-doped ceria cathodes. *Solid State Ionics* 179(17–18):647–660
- De S (1962) Groot and P. North Holland Publishing Company, Amsterdam, Mazur, Non-equilibrium Thermodynamics
- Graves C, Ebbesen SD, Jensen SH, Simonsen SB, Mogensen MB (2015) Eliminating degradation in solid oxide electrochemical cells by reversible operation. *Nat Mater* 14(2):239–244
- Pandiyan A, Uthayakumar A, Subrayan R, Cha SW, Krishna Moorthy SB (2019) Review of solid oxide electrolysis cells: a clean energy strategy for hydrogen generation. *Nanomater Energy* 8(1):2–22
- Mogensen MB, Hauch A, Sun X, Chen M, Tao Y, Ebbesen SD, Hansen KV, Hendriksen PV (2017) Relation between Ni particle shape change and Ni migration in Ni–YSZ electrodes—a hypothesis. *Fuel cells* 17(4):434–441
- Park S, Kim Y, Han H, Chung YS, Yoon W, Choi J, Kim WB (2019) In situ exsolved Co nanoparticles on Ruddlesden-Popper material as highly active catalyst for CO2 electrolysis to CO. *Appl Catal B* 248:147–156
- Zheng Y, Wang J, Yu B, Zhang W, Chen J, Qiao J, Zhang J (2017) A review of high temperature co-electrolysis of H 2 O and CO 2 to produce sustainable fuels using solid oxide electrolysis cells (SOECs): advanced materials and technology. *Chem Soc Rev* 46(5):1427–1463
- Lugo VR, Mondragón-Galicia G, Gutiérrez-Martínez A, Gutiérrez-Wing C, González OR, López P, Salinas-Hernández P, Tzompantzi F, Valderrama MIR, Pérez-Hernández R (2020) Pt–Ni/ZnO-rod catalysts for hydrogen production by steam reforming of methanol with oxygen. *RSC Adv* 10(68):41315–41323
- Shtyka O, Dimitrova Z, Ciesielski R, Kedziora A, Mitukiewicz G, Leyko J, Maniukiewicz W, Czyłkowska A, Maniecki T (2021) Steam reforming of ethanol for hydrogen production: influence of catalyst composition (Ni/Al 2 O 3, Ni/Al 2 O 3–CeO 2, Ni/Al 2 O 3–ZnO) and process conditions. *React Kinet Mech Catal* 132(2):907–919
- Pérez-Larios A, Lopez R, Hernandez-Gordillo A, Tzompantzi F, Gómez R, Torres-Guerra L (2012) Improved hydrogen production from water splitting using TiO2–ZnO mixed oxides photocatalysts. *Fuel* 100:139–143
- Steinfeld A (2002) Solar hydrogen production via a two-step water-splitting thermochemical cycle based on Zn/ZnO redox reactions. *Int J Hydrogen Energy* 27(6):611–619
- Kim D, Yong K (2021) Boron doping induced charge transfer switching of a C3N4/ZnO photocatalyst from Z-scheme to type

- II to enhance photocatalytic hydrogen production. *Appl Catal B: Environ* 282:119538
25. Zhou J, Ma H, Liu C, Zhang H, Ying W (2019) High temperature methanation over Ni catalysts supported on high surface area $\text{Zn}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$: influence on Zn loading. *Int J Hydrogen Energy* 44(26):13253–13261
 26. Lee YH, Lee D-W, Kim H, Choi HS, Lee K-Y (2015) Fe–Zn catalysts for the production of high-calorie synthetic natural gas. *Fuel* 159:259–268
 27. Le TA, Kim J, Kang JK, Park ED (2020) CO and CO₂ methanation over M (MMn, Ce, Zr, Mg, K, Zn, or V)-promoted Ni/Al@Al₂O₃ catalysts. *Catal Today* 348:80–88
 28. Dias YR, Perez-Lopez OW (2021) CO₂ conversion to methane using Ni/SiO₂ catalysts promoted by Fe, Co and Zn. *J Environ Chem Eng* 9(1):104629
 29. Frontera P, Macario A, Ferraro M, Antonucci P (2017) Supported catalysts for CO₂ methanation: a review. *Catalysts* 7(2):59
 30. Wang W, Li X, Zhang Y, Zhang R, Ge H, Bi J, Tang M (2017) Strong metal–support interactions between Ni and ZnO particles and their effect on the methanation performance of Ni/ZnO. *Catal Sci Technol* 7(19):4413–4421
 31. Heckelsberg LF, Calrk A, Bailey GC (1956) Electrical conductivity and catalytic activity of zinc oxide. *J Phys Chem* 60(5):559–561
 32. Biswas S, Kulkarni AP, Fini D, Giddey S, Bhattacharya S (2021) In situ synthesis of methane using Ag–GDC composite electrodes in a tubular solid oxide electrolytic cell: new insight into the role of oxide ion removal. *Sustain Energy Fuels* 5(7):2055–2064
 33. Biswas S, Kulkarni AP, Fini D, Rathore SS, Seeber A, Giddey S, Bhattacharya S (2021) Catalyst-induced enhancement of direct methane synthesis in solid oxide electrolyser. *Electrochimica Acta*:138934
 34. Fini D, Badwal SP, Giddey S, Kulkarni AP, Bhattacharya S (2018) Evaluation of Sc₂O₃–CeO₂–ZrO₂ electrolyte-based tubular fuel cells using activated charcoal and hydrogen fuels. *Electrochim Acta* 259:143–150
 35. Mizusaki J, Tagawa H, Miyaki Y, Yamauchi S, Fueki K, Koshiro I, Hirano K (1992) Kinetics of the electrode reaction at the CO–CO₂, porous Pt/stabilized zirconia interface. *Solid State Ionics* 53:126–134
 36. Mahmood A, Bano S, Yu JH, Lee KH (2019) Performance evaluation of SOEC for CO₂/H₂O co-electrolysis: Considering the effect of cathode thickness. *J CO₂ Util* 33:114–120
 37. Yue X, Irvine JT (2012) Impedance studies on LSCM/GDC cathode for high temperature CO₂ electrolysis. *Electrochem Solid State Lett* 15(3):B31
 38. Moussaoui H, Sharma R, Debayle J, Gavet Y, Delette G, Laurencin J (2019) Microstructural correlations for specific surface area and triple phase boundary length for composite electrodes of solid oxide cells. *J Power Sources* 412:736–748
 39. Chen S, Abdel-Mageed AM, Mochizuki C, Ishida T, Murayama T, Rabeah J, Parlinska-Wojtan M, Brückner A, Behm R Jr (2021) Controlling the O-vacancy formation and performance of Au/ZnO catalysts in CO₂ reduction to methanol by the ZnO particle size. *ACS Catal* 11:9022–9033
 40. Tak Y, Yong K (2005) Controlled growth of well-aligned ZnO nanorod array using a novel solution method. *J Phys Chem B* 109(41):19263–19269
 41. Zhang N, Yi R, Shi R, Gao G, Chen G, Liu X (2009) Novel rose-like ZnO nanoflowers synthesized by chemical vapor deposition. *Mater Lett* 63(3–4):496–499
 42. Pomfret MB, Stoltz C, Varughese B, Walker RA (2005) Structural and compositional characterization of yttria-stabilized zirconia: evidence of surface-stabilized, low-valence metal species. *Anal Chem* 77(6):1791–1795

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.