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

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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 (ZnOmix–Ag cathode) and the other one where Ag cathode was infiltrated with a zinc nitrate solution (ZnOinf–Ag cathode). ZnOmix–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 ZnOinf–Ag cathode, most of CO generation took place through RWGS reaction, but for ZnOmix–Ag cathode, it was the synergistic effect of both RWGS reaction and CO₂ electrolysis. Although ZnOinf–Ag cathode produced trace amount of methane at higher voltages, with ZnOmix–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
ZnO is a semiconductor material that has not been evaluated so far as a cathode material for CO₂ electroreduction to CO or methane. It has been widely investigated as a support material for H₂ production via steam reforming of ethanol and methanol [20, 21], and as a photocatalyst for splitting water to ethanol and methanol [20, 21]. 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 CO₂ electrolysis and steam/CO₂ co-electrolysis [3, 18, 19].

Contrarily, Dias et al. [28] reported CO₂ conversion of ~100% at 400 °C and 1 bar but low methane selectivity. Contrarily, Dias et al. [28] reported CO₂ conversion of 50% with methane selectivity of 80% with Zn promoted Ni/SiO₂. Based on the above reports, we have investigated the effect of presence of ZnO in the cathode on CO₂ conversion while electrolysing dry CO₂ as well as an H₂/CO₂ (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 O₂ 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 (Al₂O₃). 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 was infiltrated with a Zn(NO₃)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 CO₂ and H₂/CO₂ 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 (Gd₀.₁Ce₀.₉O₂₋₅) 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 (ZnOinf –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% GdCeO₂₋₅ (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(NO₃)₂·6H₂O (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.
For fabricating the ZnO mixed Ag cathode (ZnO\textsubscript{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 \(~40 \mu m\) thick with an effective cell area of 33 cm\(^2\). One millimetre thick Ag wires was 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\textsubscript{inf}–Ag cathode and the other one with ZnO\textsubscript{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 CuK\(_\alpha\) radiation (40 kV, 40 mA) equipped with a Lynx Eye XE-T detector. The sample was scanned over the 20 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 EVA\textsuperscript{TM}5. Crystalline phases were identified using the ICDD-JCPDS powder diffraction database. Rietveld analyses were performed on the data using the Bruker TOPAS\textsuperscript{TM} 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
Results and discussion

Performance of two different ZnO-based cathodes towards CO₂ electrolysis

Two tube cells, ZnO_{inf} –Ag|8YSZ|AG-GDC and ZnO_{inf} –Ag|8YSZ|AG-GDC, were tested at 500, 600 and 700 °C in dry CO₂ atmosphere. Figure 2a, b depict the impedance spectra recorded with ZnO_{inf} –Ag cathode at OCV and at 1.5 V, respectively. As expected, at both OCV and 1.5 V, ohmic resistance ($R_{\text{ohm}}$) and polarization resistance ($R_{\text{pol}}$) decreased with temperature, indicating higher ionic conductivity and improved cell kinetics at elevated temperature. However, at any particular temperature, $R_{\text{pol}}$ 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 CO₂ electrolysis. This agrees with the impedance trends where a substantial increase in $R_{\text{pol}}$ from OCV to 1.5 V has been observed (Table 1). With ZnO_{mix}–Ag cathode, current density at any particular voltage was almost 20 times higher (Fig. 2d) than ZnO_{inf} –Ag cathode. Additionally, for the ZnO_{mix}–Ag cathode, current density increased monotonically with temperature, whereas ZnO_{inf} –Ag cathode showed no significant increase in current density until above 1.4 V at all temperatures. Also, unlike ZnO_{inf} –Ag cathode, with ZnO_{mix}–Ag cathode $R_{\text{pol}}$ decreased upon increasing the applied potential from OCV to 1.5 V (Fig. 2e). In fact, at 1.5 V, $R_{\text{pol}}$ values at all three temperatures were smaller than the corresponding $R_{\text{ohm}}$ values, indicating that the process was mostly ohmic controlled, whereas, for ZnO_{inf} –Ag cathode, the process was polarization controlled.

![Figure 2](image-url)

**Fig. 2** Impedance spectra recorded with ZnO_{inf} –Ag cathode while electrolyzing dry CO₂ 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 ZnO_{mix}–Ag cathode while electrolyzing dry CO₂ 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.

| Cathode     | Temperature (°C) | Applied voltage (V) | $R_{\text{ohm}}$ (Ω-cm²) | $R_{\text{pol}}$ (Ω-cm²) | CO₂ (%)  | CO (%)  | CO₂ conversion (%) |
|-------------|------------------|---------------------|---------------------------|--------------------------|----------|---------|-------------------|
| ZnO_{inf}–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              |
| ZnO_{mix}–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              |
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 ZnO\textsubscript{mix}–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 (\(R_{\text{act}}\)) of the electrodes and concentration polarization (\(R_{\text{con}}\)) [13, 36, 37], whereas the tail resembling Warburg impedance could be due to diffusion resistance and resistance to CO\textsubscript{2}-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, \(R_{\text{act}}\) and \(R_{\text{con}}\) were the major contributors to \(R_{\text{pol}}\), whereas with increase in temperature diffusion and surface-reduction of CO\textsubscript{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 ZnO\textsubscript{mix}–Ag cathode (Fig. 2e) at OCV consisted of a single arc that shrank 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 \(R_{\text{ohm}}\) and \(R_{\text{pol}}\) values obtained with the two different cathodes (Table 1) revealed that both exhibited very similar \(R_{\text{ohm}}\) values at any particular temperature confirming reproducible cell fabrication. However, \(R_{\text{pol}}\) values widely varied between ZnO\textsubscript{mix}–Ag and ZnO\textsubscript{inf}–Ag cathodes. At OCV, \(R_{\text{pol}}\) was slightly higher for ZnO\textsubscript{mix}–Ag, and this was consistently observed at all three test temperatures. Contrarily, at 1.5 V, \(R_{\text{pol}}\) with ZnO\textsubscript{mix}–Ag cathode was orders of magnitude less than that for ZnO\textsubscript{inf}–Ag cathode. Since the anode was the same (Ag-GDC) for both the tube cells, we surmise that the disparity in the \(R_{\text{pol}}\) 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\textsubscript{2} conversion at 500 °C at OCV as well as at 1.5 V. However, at 600 and 700 °C at OCV, CO\textsubscript{2} conversion with ZnO\textsubscript{inf}–Ag cathode was respectively 0.07 and 0.99% that increased by ~1.2 times with ZnO\textsubscript{mix}–Ag cathode. Since electrolysis could not have occurred under no-load conditions, such CO\textsubscript{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 ZnO\textsubscript{mix}–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\textsubscript{2} conversion with ZnO\textsubscript{inf}–Ag cathode increased to 0.33 and 1.71% at 600 and 700 °C, respectively. With ZnO\textsubscript{mix}–Ag cathode, the corresponding CO\textsubscript{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\textsubscript{2} electrolysis where ZnO\textsubscript{mix}–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\textsubscript{2}/CO\textsubscript{2} electrolysis**

The same two tube cells were tested at 500, 600 and 700 °C in H\textsubscript{2}/CO\textsubscript{2} (4:1 v/v) atmosphere. The V–I curves with ZnO\textsubscript{inf}–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 mA cm\(^{-2}\) 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\textsubscript{2} atmosphere discussed in the “Performance of two different ZnO-based cathodes towards CO\textsubscript{2} electrolysis”. \(R_{\text{ohm}}\) was almost constant under all applied potentials at a particular temperature (Table 2), but \(R_{\text{pol}}\) first increased and then gradually decreased. For instance, at 500 °C, \(R_{\text{pol}}\) increased from 78.88 Ω·cm\(^{-2}\) at OCV to 2359.75 Ω·cm\(^{-2}\) at 1.5 V and then started reducing. At 600 and 700 °C, \(R_{\text{pol}}\) 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\textsubscript{2}/CO\textsubscript{2} electrolysis [33].

Contrarily, with ZnO\textsubscript{mix}–Ag cathode, the \(R_{\text{pol}}\) at all test temperatures dropped systematically from OCV till the maximum applied potential of 1.9 V (Fig. 4a, b and c). Compared to ZnO\textsubscript{inf}–Ag cathode, ZnO\textsubscript{mix}–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\textsubscript{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, \(R_{\text{pol}}\) recorded with ZnO\textsubscript{mix}–Ag cathode was almost two orders of magnitude lesser than what had been obtained with ZnO\textsubscript{inf}–Ag.
cathode in spite of $R_{\text{ohm}}$ being similar for both. The resulting current density (Fig. 4d) was also almost two orders of magnitude higher than ZnO$_{\text{inf}}$–Ag cathode.

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

Table 2 shows CO%, CH$_4$% and 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).

\[
\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \quad (\Delta H_{1023} = 41.2 \text{ kJ/mol}) \quad (1)
\]

\[
\text{CO}_2 + 2\text{e}^- = \text{CO} + \text{O}_2^- \quad (\Delta H_{1023} = 282 \text{ kJ/mol}) \quad (2)
\]

\[
\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} \quad (\Delta H_{1023} = 206.1 \text{ kJ/mol}) \quad (3)
\]

\[
\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2 \quad (\Delta H_{1023} = 206.1 \text{ kJ/mol}) \quad (4)
\]

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 ZnO$_{\text{mix}}$–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, CO% with ZnO$_{\text{mix}}$–Ag cathode was almost two to four times higher than what had been generated with ZnO$_{\text{inf}}$–Ag cathode. Similar trends are reflected in the CO$_2$ conversion as well (Fig. 5a). As can be seen from Fig. 5a, b, for ZnO$_{\text{inf}}$–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 ZnO$_{\text{mix}}$–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 ZnO$_{\text{inf}}$–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 ZnO$_{\text{inf}}$–Ag nor ZnO$_{\text{mix}}$–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, ZnO$_{\text{inf}}$–Ag and ZnO$_{\text{mix}}$–Ag cathodes exhibited 1.93 and 5.62% CO$_2$ conversion, respectively. While for ZnO$_{\text{inf}}$–Ag cathode, most of the conversion took place through RWGS reaction, for ZnO$_{\text{mix}}$–Ag cathode, it was the synergistic effect of both RWGS reaction and

Fig. 3 Voltage-current curves recorded with ZnO$_{\text{inf}}$–Ag cathode while electrolysising 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.
CO₂ electrolysis. Similarly, at 600 and 700 °C, CO₂ conversion with ZnOₘᵢₓ–Ag cathode was much higher in H₂/CO₂ compared to dry CO₂ under the same applied potential. The higher CO₂ electrolysis efficacy of the same material (ZnOₘᵢₓ–Ag) in H₂/CO₂ atmosphere can be attributed to H₂ 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 ZnOₐᵢᶠ–Ag cathode, trace amounts of methane were obtained (Table 2) but with ZnOₘᵢₓ–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 had been established between ZnO and Ag, resulting in the suppression of methanation. The effect was more pronounced for ZnOₘᵢₓ–Ag cathode where ZnO particles were uniformly distributed throughout the cathode surface. Thus, ZnOₘᵢₓ–Ag cathode generated no methane at all.

| Cathode      | Temperature (°C) | Applied voltage (V) | Current (mA cm⁻²) | Rₜₜₜ (Ω·cm²⁻¹) | Rₚₒₜ (Ω·cm²⁻¹) | CO₂ (%) | CH₄ (%) | CO (%) |
|--------------|------------------|---------------------|-------------------|----------------|----------------|---------|--------|-------|
| ZnOₐᵢᶠ–Ag   | 500 OCV          | 0.00                | 42.56             | 78.88          | 19.82          | 0.00    | 0.21   |
|              | 1.3              | 0.21                | 42.30             | 1559.70        | 19.75          | 0.00    | 0.23   |
|              | 1.5              | 0.46                | 42.25             | 2359.75        | 19.61          | 0.00    | 0.29   |
|              | 1.7              | 0.57                | 42.17             | 2059.83        | 19.45          | 0.00    | 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          | 0.00    | 0.91   |
|              | 1.3              | 0.31                | 9.89              | 1241.11        | 19.01          | 0.00    | 0.96   |
|              | 1.5              | 1.01                | 9.67              | 851.33         | 18.99          | 0.00    | 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   | 1.45   |
|              | 1.9              | 3.75                | 9.28              | 46.72          | 17.81          | 0.019   | 2.16   |
| ZnOₘᵢₓ–Ag   | 500 OCV          | 0.00                | 4.39              | 8.74           | 18.35          | 0.00    | 1.72   |
|              | 1.3              | 0.44                | 4.32              | 185.68         | 18.08          | 0.00    | 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   |
|              | 600 OCV          | 0.00                | 40.77             | 41.31          | 19.57          | 0.00    | 0.43   |
|              | 1.3              | 20.62               | 40.36             | 40.81          | 19.28          | 0.00    | 0.72   |
|              | 1.5              | 23.99               | 40.08             | 14.78          | 18.88          | 0.00    | 1.12   |
|              | 1.7              | 27.66               | 39.86             | 6.69           | 17.88          | 0.00    | 2.12   |
|              | 1.9              | 31.69               | 39.59             | 5.40           | 16.82          | 0.00    | 3.18   |
|              | 700 OCV          | 0.00                | 10.24             | 42.75          | 18.02          | 0.00    | 1.98   |
|              | 1.3              | 42.06               | 9.58              | 38.41          | 17.53          | 0.00    | 2.47   |
|              | 1.5              | 50.06               | 9.24              | 10.67          | 16.75          | 0.00    | 3.25   |
|              | 1.7              | 58.30               | 9.15              | 5.74           | 15.41          | 0.00    | 4.59   |
|              | 1.9              | 63.00               | 9.01              | 2.64           | 13.65          | 0.00    | 6.35   |
|              | 700 OCV          | 0.00                | 3.94              | 11.06          | 16.45          | 0.00    | 3.55   |
|              | 1.3              | 89.93               | 3.85              | 1.15           | 14.99          | 0.00    | 5.01   |
|              | 1.5              | 108.11              | 3.80              | 0.83           | 12.78          | 0.00    | 7.22   |
|              | 1.7              | 122.90              | 3.78              | 0.28           | 10.48          | 0.00    | 9.52   |
imaging of fresh and tested cathodes also supports this conjecture as discussed later in the “SEM characterization of two different ZnO-based cathodes”.

**Fig. 4** Impedance spectra recorded with ZnO$_{\text{inf}}$–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

**Fig. 5** CO$_2$ a and H$_2$ b conversions obtained with ZnO$_{\text{inf}}$–Ag and ZnO$_{\text{mix}}$–Ag cathodes under H$_2$/CO$_2$ atmosphere at different loaded conditions between 500 and 700 °C

**Fig. 6** SEM image of fresh ZnO$_{\text{inf}}$–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 ZnO$_{\text{inf}}$–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

**SEM characterization of two different ZnO-based cathodes**

The fresh ZnO$_{\text{inf}}$–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
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 by adjacent Ag particles (Fig. 7g). This is clearly perceptible form 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) 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...
cathode). In case of ZnO\textsubscript{inf}–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\textsubscript{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 ZnO\textsubscript{mix}–Ag cathode varied in size from 100 to 500 nm as opposed to a size range of 100 to 200 nm for ZnO\textsubscript{inf}–Ag. The larger particle size could be another reason behind the interaction between Zn and Ag envisaged with ZnO\textsubscript{mix}–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 ZnO\textsubscript{inf}–Ag cathode (Fig. 9a), the major phases detected were hexagonal ZnO and cubic Ag along with cubic Y\textsubscript{0.06}Zr\textsubscript{0.94}O\textsubscript{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 ZnO\textsubscript{mix}–Ag cathode depicted hexagonal ZnO, cubic Ag and cubic Y\textsubscript{0.06}Zr\textsubscript{0.94}O\textsubscript{1.97} as the major phases. Compared to fresh ZnO\textsubscript{inf}–Ag cathode, the ZnO peaks were more prominent for fresh ZnO\textsubscript{mix}–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 ZnO\textsubscript{mix}–Ag cathode showed sharp reflections from ZnO at 31.7, 34.5 and 36.4°, whereas fresh ZnO\textsubscript{inf}–Ag cathode exhibited stunted reflections. For tested ZnO\textsubscript{mix}–Ag cathode, ZnO peaks became shorter and broader compared to fresh cathode, indicating particle size reduction, and for tested ZnO\textsubscript{inf}–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 ZnO\textsubscript{inf}–Ag cathode, ZnO crystallite
size was 59 nm that reduced to 20 nm for tested cathode. Contrarily, for fresh ZnOmix–Ag cathode, ZnO crystallite size was 110 nm (almost double that of fresh ZnOinf–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 (H2/CO2) 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 ZnOmix–Ag cathode, Ag crystallite size reduced from 225 to 46 nm. For ZnOinf–Ag cathode, Ag crystallite size reduced from ~1000 to 170 nm. Similarly, the Y0.06Zr0.94O1.97 peaks also broadened and became stunted for tested cathodes indicating crystallite size reduction. The Y0.06Zr0.94O1.97 reflections from both ZnOmix–Ag and ZnOinf–Ag tested cathodes exhibited slight peak shift to lower angle, which denotes lattice expansion. One possibility could be dissolution of Zn2+ 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 H2/CO2 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 H2 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 CO2 reduction in a single temperature SOEC by electrolysing CO2 alone and a mixture of H2/CO2 (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 (ZnOinf–Ag cathode), and the other method where ZnO nanopowder was mixed with Ag powder to prepare the cathode ink (ZnOmix–Ag cathode). SEM imaging coupled with EDX mapping revealed that ZnO distribution was more uniform in ZnOmix–Ag cathode, whereas in ZnOinf–Ag cathode the ZnO particles formed sporadic clusters of self-assembled structures. As a result, oxygen vacancy distribution (upon exposure to H2/CO2) was more uniform on ZnOmix–Ag cathode. This was manifested by a monotonically decreasing Rp with voltage for the ZnOmix–Ag cathode. Contrarily, with ZnOinf–Ag cathode, Rp first increased dramatically from OCV to a certain applied voltage and then decreased. Consequently, CO production at any temperature and voltage with ZnOmix–Ag cathode was almost thrice that with ZnOinf–Ag cathode. It is worth mentioning that with CO2 alone as well, the conversions of CO2 were more than twice at 600 °C and 700 °C for ZnOmix–Ag cathode compared to ZnOinf–Ag cathode. The CO2 and H2 conversion trends revealed that for ZnOinf–Ag cathode, most of CO generation took place through RWGS reaction, but for ZnOmix–Ag cathode, it was the synergistic effect of both RWGS reaction and CO2 electrolysis. Maximum CO2 and H2 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 CO2 conversion to CO in a reducing environment, i.e. in the presence of H2. It was also observed that ZnOinf–Ag cathode produced trace amount of methane at higher voltages, but with ZnOmix–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 ZnO\textsubscript{mix}−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 ZnO\textsubscript{mix}−Ag cathode but not on the ZnO\textsubscript{ir}−Ag. Nonetheless, there is scope for further investigation through electron paramagnetic resonance analysis and in operando Fourier transform infrared spectroscopy.

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**Declarations**

**Conflict of interest**  The authors declare no competing interests.

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