

"Navigating the impurity-obstructive electronegative interfacial carbonate on the hybrid ceria/carbonate interface for solid oxide fuel cells."

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ABSTRACT

Ceria-carbonate composite electrolytes have received much attention in recent years for application in low-temperature solid oxide fuel cells (LT-SOFCs). The principal advantage of carbonate in composite electrolytes is its role in conductivity enhancement, proposed through several different mechanisms. This study navigates the scarcely studied obstruction caused by electronegative interfacial carbonate to impurity intrusion into the ceria lattice, with some interesting facts being noted. The methodically examined structure-property relationship of systematically annealed doped ceria, incorporated with carbonate at the grain boundary region, revealed a change in the nature of carbonate especially when annealed between 600–800 °C. Owing to the electronegativity difference between carbonate and host ceria, the added impurities (magnesium and lithium) showed preferential bonding with the interfacial carbonate evidenced by a change in peak positions for carbonate in the Raman spectra. This was further supported by an increase in defect concentration for samples that were annealed at 600 °C, which unexpectedly declined when the annealing temperature was increased to 800 °C, as demonstrated by the quantitative analysis of Raman spectra. Electrochemical impedance spectroscopy (EIS) indicated lower activation energy in the presence of carbonate, leading to reduced electrolyte resistance, thereby resulting in enhanced interfacial conductivity. Volatilizing the interfacial carbonate by annealing the prepared samples at higher temperatures (1200 °C) resulted in a second-stage incorporation of impurities, especially lithium, in the ceria phase. The fuel cell performance of selected high-temperature annealed samples showed impressive results and suitability for fuel cell applications provided the materials prove to display long-term stability. Therefore, long-term stability studies with microstructural characterization would be needed as the carbonate-containing electrolytes may show residual porosity after sintering, which could affect gas-tightness and long-term stability.

1. Introduction

The continuously increasing energy demand calls for a sustainable energy technology capable of producing energy cleanly, efficiently, and economically [1]. In response, solid oxide fuel cells (SOFCs) emerged as a promising technology with the ability to produce clean energy with high efficiency. However, this requires high operating temperatures (800–1000 °C) which are a major hindrance to their commercialization. Strategies to enhance the performance through changes in material design are in progress; thus, significant research is being done to find alternative electrolyte materials able to work effectively in the low-temperature regime (600 °C or lower) [2]. Traditionally used

yttria-stabilized zirconia (YSZ) gives acceptable ionic conduction at 800 °C or above, bringing associated problems like faster material degradation due to high-temperature operation, leading to increased maintenance and ultimately higher costs [3,4]. Efforts to replace YSZ have resulted in the introduction of ceria-based electrolytes for SOFCs.

Pure ceria is a poor ionic conductor; however, when doped with an aliovalent cation of comparable ionic radius, it shows fast ion conduction at 600 °C or lower [5]. 20 mol% samarium (Sm^{3+} ; $r = 0.1079$ nm) doped ceria (Ce^{4+} ; $r = 0.097$ nm), commonly known as SDC, has emerged as a good electrolyte for SOFCs due to its increased ionic conduction at low temperatures, superior to that of YSZ [6].

Unfortunately, the rare earth constituent metals make SDC costly, a

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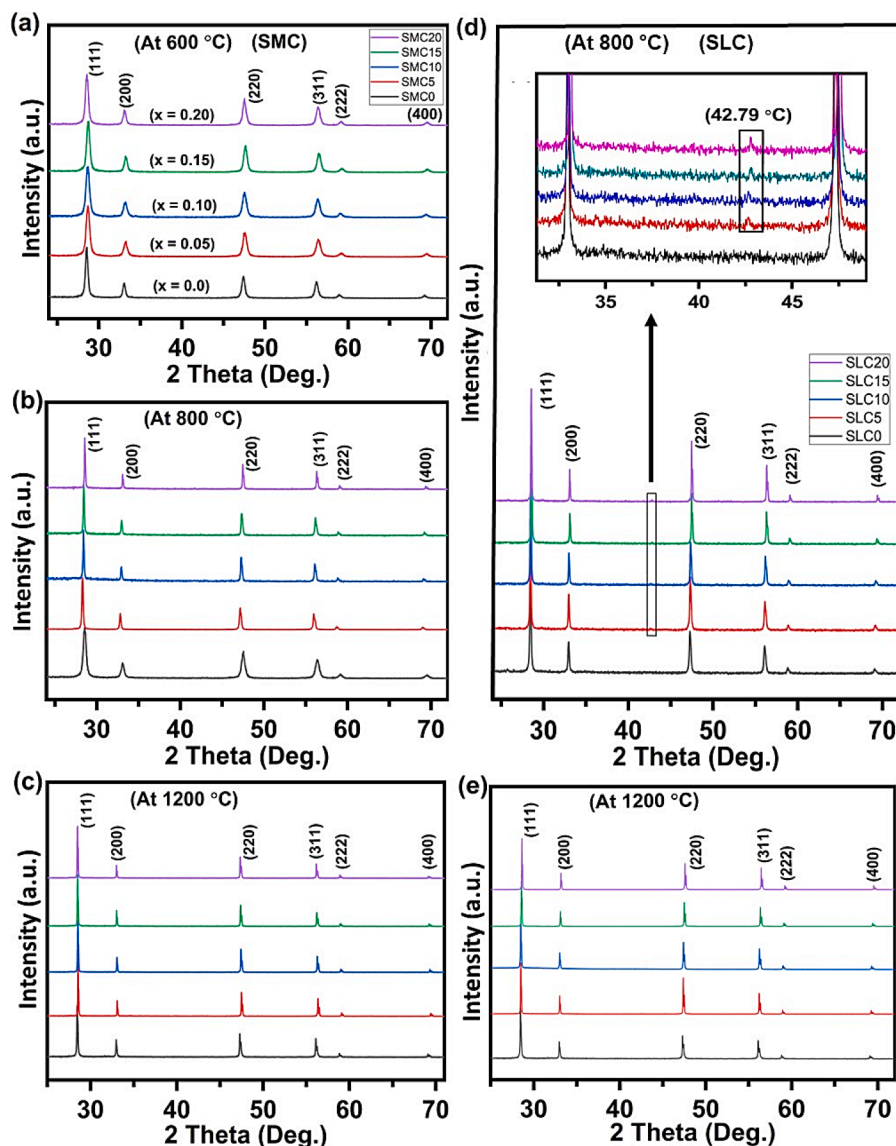


Fig. 1. Room temperature XRD patterns of (a–c) SMC powders annealed at 600 °C, 800 °C and 1200 °C, (d, e) SLC powders annealed at 800 °C and 1200 °C, respectively. The weak peak emphasised at 42.79° corresponds to a minor carbonate phase.

Table 1

Lattice parameters (a in Å) of SMC and SLC powders with varied dopant concentrations that were annealed at different temperatures.

Sample	600 °C	800 °C	1200 °C	Sample	800 °C	1200 °C
SMC0	5.422	5.435	5.432	SLC0	5.435	5.432
SMC5	5.405	5.429	5.428	SLC5	5.428	5.429
SMC10	5.399	5.422	5.418	SLC10	5.423	5.423
SMC15	5.393	5.413	5.419	SLC15	5.410	5.410
SMC20	5.405	5.406	5.408	SLC20	5.410	5.401

bottleneck to commercialization. In efforts to reduce cost and improve performance, the co-doping approach was introduced to replace some of the rare earth metals with more cost effective and abundant non-rare earth metals (such as alkali metals, alkaline earth metals and some transition metals) [6–8]. Resultantly, comparable or even higher ionic conductivities than SDC have been reported for the co-doped ceria [7,8], but have not always adequately addressed the structure-property relationship; for example, successful partial replacement of Sm^{3+} by Mg^{2+} [7] or Li^+ [6] was cited based on cell parameter variation only.

Different synthesis routes have been employed to prepare SDC [7,

9–11]. Since the first report introducing the novel core-shell SDC/amorphous Na_2CO_3 concept by Wang et al [12], carbonate co-precipitation has received much attention, followed by many papers employing this two-phase concept, as cited in a review by Raza et al [5]. Apart from benefits like easy handling, high yield, and low calcination temperature, the carbonate was suggested to be beneficial in conductivity enhancement for SDC/ Na_2CO_3 , acquiring an improved conductivity value of 0.1 S/cm above 300 °C, making it a superionic conductor [12]. Additional useful aspects due to the presence of carbonate are highlighted in the review by Fan et al [13], and include its function as a sintering aid and pore filler to improve density, an electrode/electrolyte glue, an electron insulator, and an oxygen reduction reaction accelerator.

There is a debate concerning the mechanism of ion transport through composite electrolyte, particularly through the carbonate phase. Wang et al [12], and Raza et al [8], based their explanations on solid-state theory, and Zhang et al [14], applied the space charge model. Tong et al [15], proposed a mechanism using a cooperative ‘cogwheel’ scheme to indicate the rotation, breaking, and reformation of $\text{O} - \text{CO}_3^{2-}$ bond during oxide ion transport through molten carbonate, coupled with density functional theory (DFT) calculations, which will be depicted

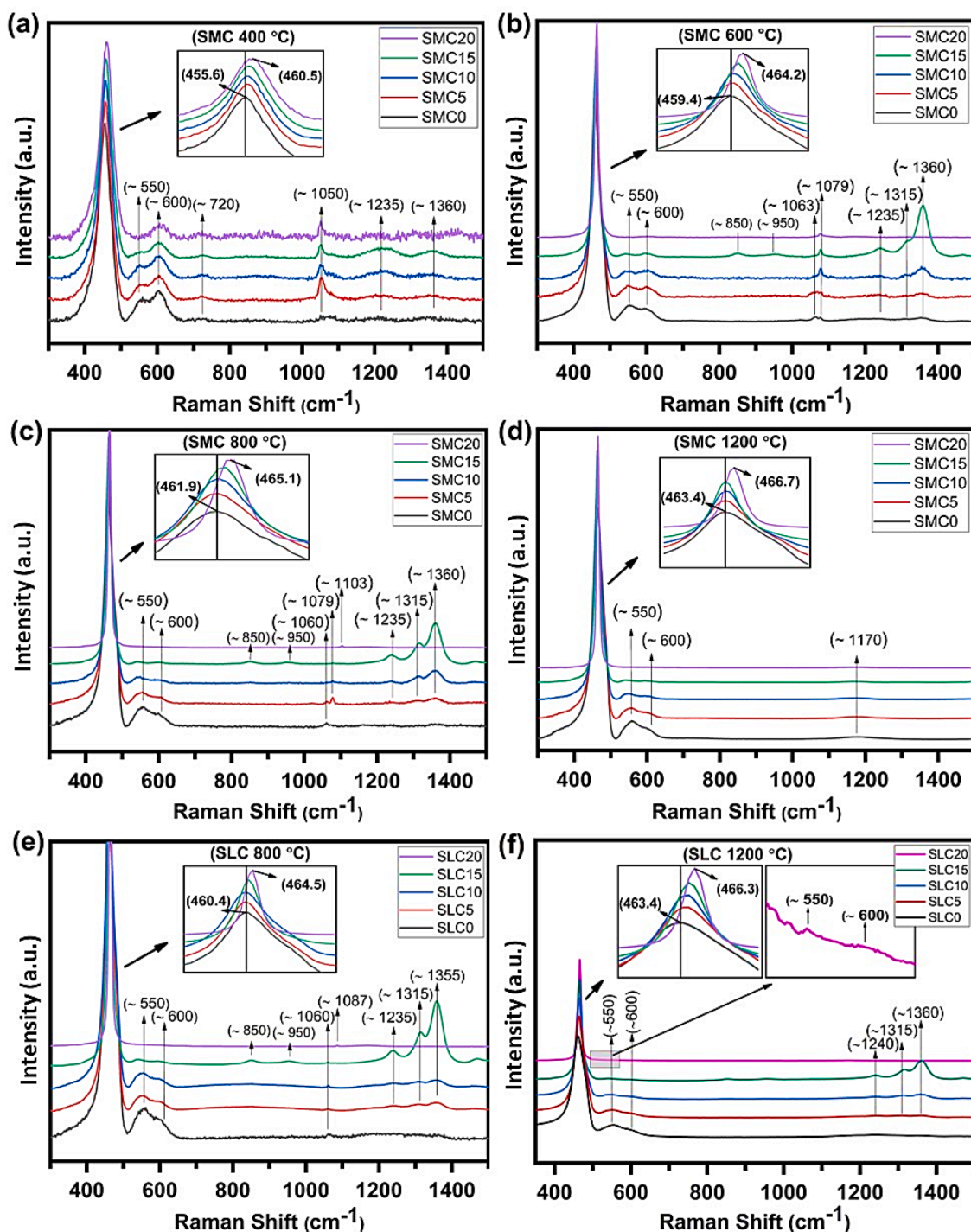


Fig. 2. Raman spectra of SMC powders (SMC0–SMC20) annealed at (a) 400 °C, (b) 600 °C (c) 800 °C and (d) 1200 °C while (e) and (f) show the Raman spectra of SLC powders (SLC0–SLC20) annealed at 800 °C and 1200 °C, respectively. The insets in Fig. 2 (a–f) show the F_{2g} band variation with change in stoichiometry.

Table 2

F_{2g} band positions (in cm^{-1}) of SMC and SLC powders with change in dopant concentrations and annealing temperature.

Sample	400 °C	600 °C	800 °C	1200 °C	Sample	800 °C	1200 °C
SMC0	455.6	459.4	461.9	463.4	SLC0	460.4	463.4
SMC5	457.1	461.1	462.6	463.4	SLC5	461.0	463.4
SMC10	457.4	461.8	462.7	463.5	SLC10	461.5	464.0
SMC15	458.3	463.2	463.9	463.6	SLC15	462.8	464.5
SMC20	460.5	464.2	465.1	465.3	SLC20	464.5	466.3

schematically later in the discussion. The mechanisms for dual or hybrid conduction of ions (H^+ and O^{2-}) through carbonate have also been proposed in different reports, including [9]. Lei et al [16]. used static and dynamic DFT calculations to show the inter-carbonate and intra-carbonate proton migration pathways. The proton transfer through the ceria-carbonate composite was also proposed using a swing model reported elsewhere [17].

In earlier reports on doped ceria-carbonate composite electrolytes, particularly co-doped with non-rare earth metals, the focus was on indicating that doping of the ceria related phase had occurred, and the nature of the carbonate phase was not further investigated as it was

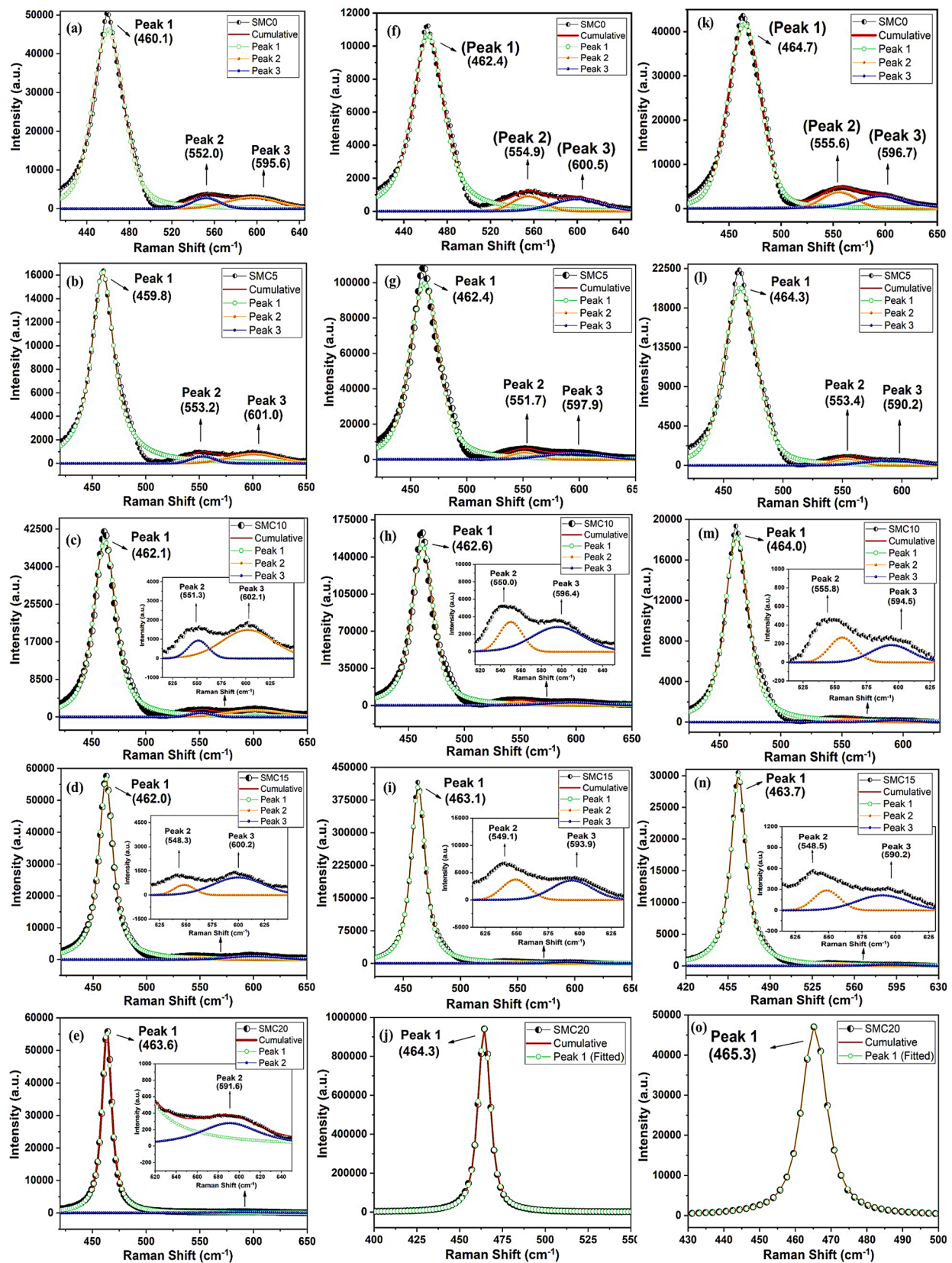


Fig. 3. Multiple peak fitted Raman spectra of SMC sample annealed at 600 °C (a-e) 800 °C (f-j), and 1200 °C (k-o), respectively.

Table 3

Defect concentration determined as the area ratio ($A_{\sim 550}/A_{F2g}$) [19] for SMC and SLC powders with change in dopant concentrations and annealing temperature.

Sample	600 °C	800 °C	1200 °C	Sample	800 °C	1200 °C
SMC0	0.069	0.078	0.078	SLC0	0.078	0.078
SMC5	0.040	0.052	0.051	SLC5	0.048	0.052
SMC10	0.039	0.029	0.023	SLC10	0.023	0.031
SMC15	0.033	0.020	0.015	SLC15	0.014	0.024
SMC20	0.010	-	-	SLC20	-	0.010

supposed to be in an amorphous form. For example, in a study on $Ce_{0.8}Sm_{0.2-x}Ca_xO_{2-8}-Na_2CO_3$ [9], the peak at $\sim 1100\text{ cm}^{-1}$ in the Raman spectra was ascribed to Na_2CO_3 . However, the ν_1 mode for Na_2CO_3 is normally close to 1083 cm^{-1} , possibly indicating the presence of some $CaCO_3$. Additionally, when focusing on the actual ceria-related phase, careful consideration should be given to the fact that not all the dopant may be incorporated into the ceria lattice. For example, when preparing $Ce_{0.8}Bi_{0.2}O_x$ and $Ce_{0.9}Bi_{0.1}O_x$ [18], the authors assigned the Raman bands at 510 cm^{-1} and 570 cm^{-1} to the generation of oxygen vacancies, indicating successful doping of Bi^{3+} into cerium. These may also reflect the possible presence of bismuth oxide related phases.

Much of the focus has been on highlighting the beneficial role of carbonate in conductivity enhancement, but the solubility of a co-dopant in the host ceria lattice, particularly that of non-rare earth metals, in the presence of carbonate has been largely ignored and needs to be more carefully investigated. A report by Uthayakumar et al [19]. is

of particular importance in this regard as it indicated that Sr^{2+} , instead of entering the ceria lattice, combines with carbonate and forms a crystalline $SrCO_3$ phase, evident from the XRD and Raman spectroscopy results.

Doping ceria with divalent cation, such as Mg^{2+} , distorts its crystal lattice and carrier transport pathways, thereby affecting its defect chemistry and transport properties. The incorporation of Mg^{2+} into ceria lattice leads to generation of oxygen vacancies, significant lattice strain and defect clustering ensue when the dopant concentration surpasses the optimal range of $\sim 10\text{--}20\text{ mol } \%$, hence impeding its ionic conductivity [20]. Due to structural changes, Mg^{2+} ions bind with nearby oxygen vacancies to form stable complexes that obstruct ion mobility, making vacancy migration more difficult [21]. Similarly, high-temperature sintering poses serious challenges to lithium containing ceramics, as Li^+ volatilizes above $\sim 800\text{ }^\circ\text{C}$, resulting in significant loss and decreasing the conductivity [22].

Keeping all this in view, to re-investigate the effect of co-dopants' incorporation into the ceria lattice, we have prepared co-doped ceria-carbonate composite electrolytes ($Ce_{0.8}Sm_{0.2-x}M_xO_{2-8}$, $M = Mg^{2+}$, Li^+ and $x = 0, 0.05, 0.1, 0.15, 0.2$) via co-precipitation. Upon systematic calcination at different temperatures, it was revealed that the co-dopants Mg^{2+} and Li^+ showed preferential bonding to carbonate, in the molten form, due to the electronegativity difference between carbonate and the host ceria lattice, and appeared to form the respective metal carbonate related phases. The effect of low- and high-temperature calcination on the structure-property relationship was also investigated.

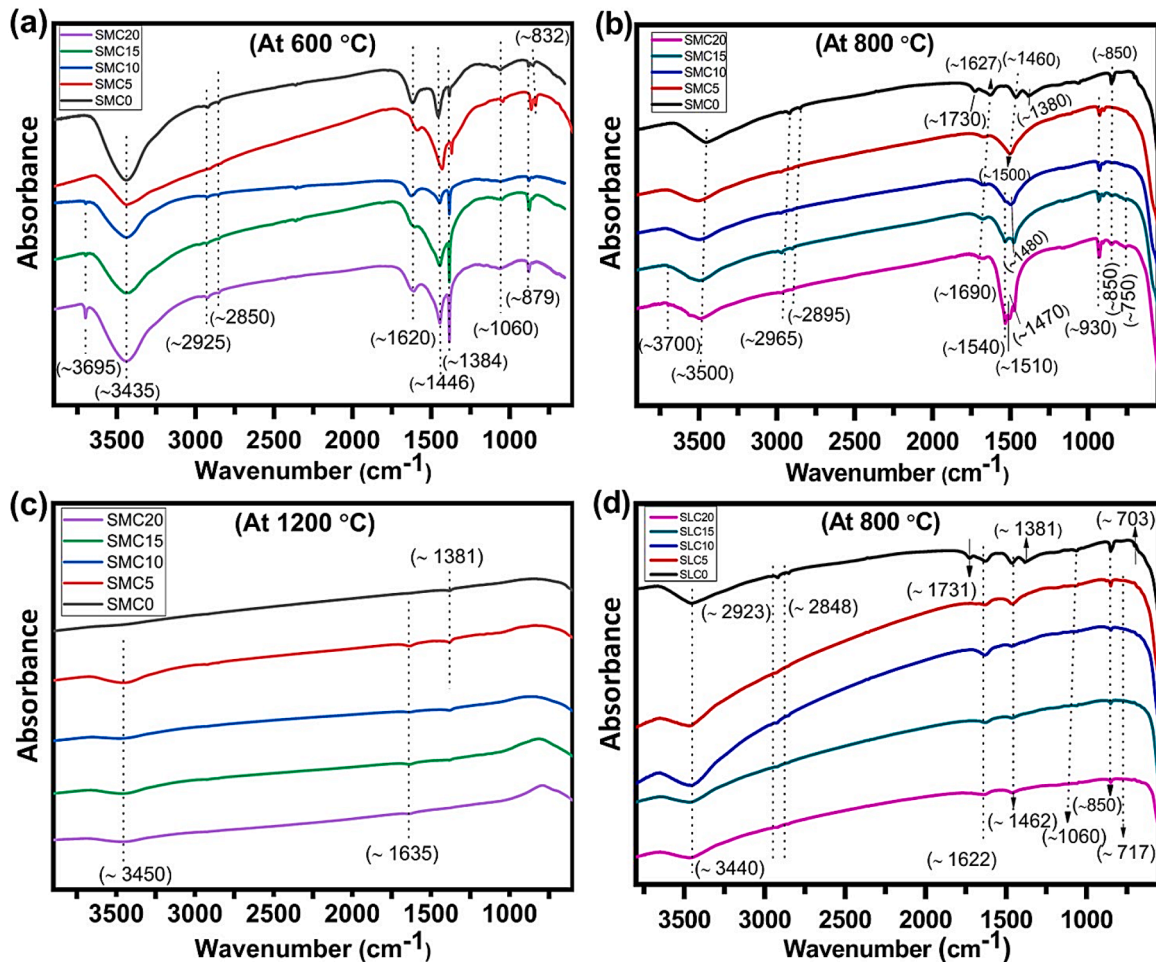


Fig. 4. FTIR spectra of SMC samples (a, b, c) annealed at 600 °C, 800 °C and 1200 °C, respectively, and (d) shows the FTIR spectra of SLC samples annealed at 800 °C.

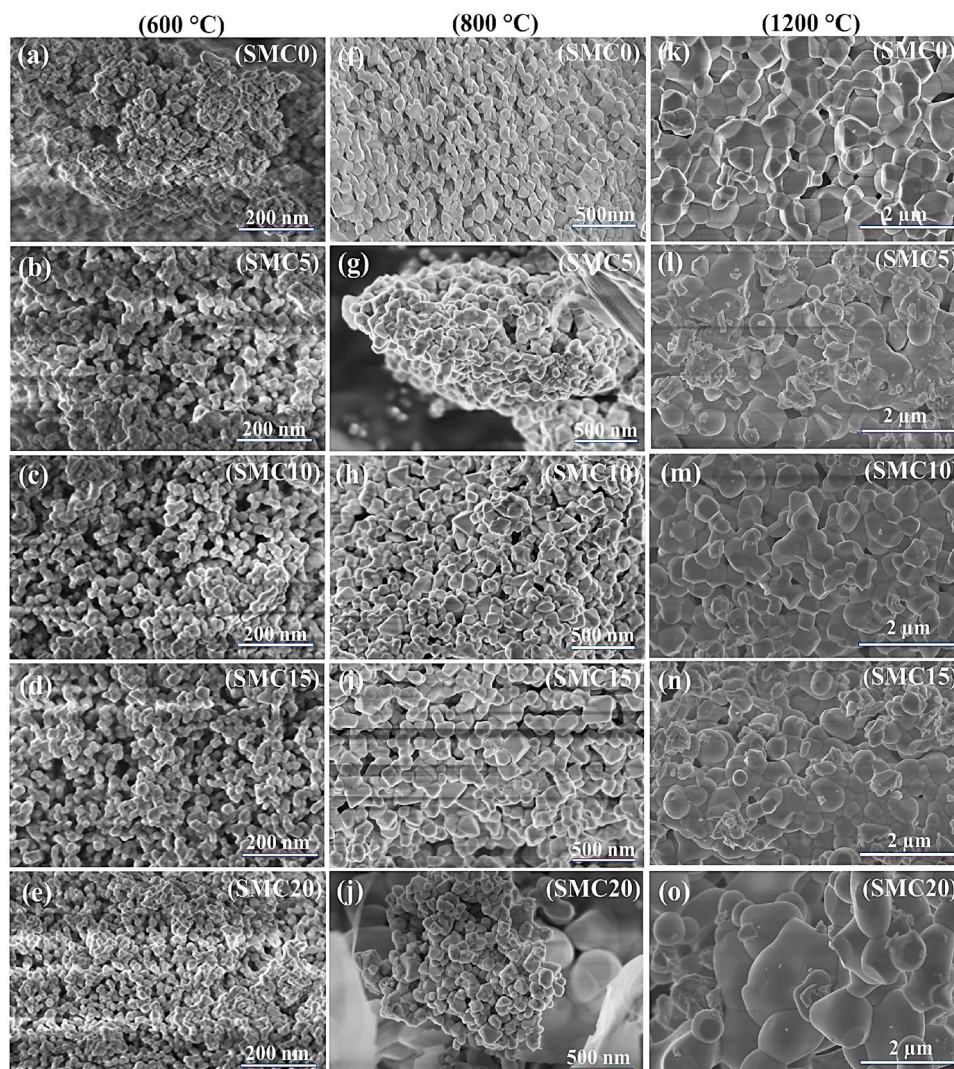


Fig. 5. SEM micrograph of SMC powders (SMC0–SMC20) annealed at 600 °C (a–e), 800 °C (f–j), and 1200 °C (k–o).

2. Experimental

2.1. Synthesis

The co-precipitation route was adopted to prepare powders of SMC and SLC (herein SMC0, SMC5, SMC10, SMC15, SMC20 for $\text{Ce}_{0.8}\text{Sm}_{0.2-x}\text{Mg}_x\text{O}_{2-8}/\text{carbonate}$ where $x = 0, 0.05, 0.1, 0.15$ and 0.2 , respectively, and SLC0, SLC5, SLC10, SLC15, SLC20 for $\text{Ce}_{0.8}\text{Sm}_{0.2-x}\text{Li}_x\text{O}_{2-8}/\text{carbonate}$). The precursors $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and LiNO_3 (Sigma Aldrich with 99.999 % purity) were mixed according to their stoichiometric amounts in de-ionised water and stirred to dissolve all salts. This was followed by the dropwise addition of 2 mol L^{-1} sodium carbonate solution (Sigma Aldrich and 99.999 % pure) to obtain white precipitates. The total metal ion to carbonate mole ratio was 1:2. The precipitates obtained were dried in an oven at 120 °C. The SMC powders were annealed at 400 °C, 600 °C, 800 °C and 1200 °C for 4 h at each step while SLC powders were only annealed at 800 °C (4 h) and 1200 °C for 4 h. The obtained samples were crushed into fine powders using a mortar and pestle for further characterisation.

2.2. Sample characterization

The crystal structure was examined using powder X-ray diffraction (XRD, Bruker D8, Germany) with Cu K_α radiation (1.54056 Å). Surface

morphology was studied using scanning electron microscopy (SEM, Hitachi S4800, Thermo Scientific Verios G4 UC and Regulus 8230 depending on availability) and transmission electron microscopy (TEM, Tecnai F20). Spectra of the powdered samples were obtained using Raman spectrometry (Renishaw inVia Reflex, $\lambda = 532 \text{ nm}$) as well as Fourier transform infrared spectroscopy (FTIR, ThermoFisher Scientific, Nicolet 6700 cm^{-1}) employing the classical KBr pellet method. To measure electrical properties, the sample powders were pressed into circular pellets (11 mm diameter and $\sim 1 \text{ mm}$ thick) at 250 MPa and sintered for 4 h at 600 °C, 800 °C, and 1200 °C, depending on the annealing temperature. Pt paste was coated on both sides for current collection. The electrical properties were determined in air over the temperature range of 550–750 °C (500–600 °C for SMC powders annealed at 600 °C), using electrochemical impedance spectroscopy (CorrTest Electrochemical and Corrosion Studio, Ver. 5.3, China) in the frequency range 0.1 Hz to 1 MHz and using an ac amplitude of 10 mV. Zview (Scribner) was used to model the data using equivalent circuits. Thermal studies were done using a PerkinElmer Diamond TGA/DTA. The sample was heated from room temperature till 1000 °C at a rate of $10^\circ\text{C min}^{-1}$ while flowing nitrogen (50 ml min^{-1}) to purge the system.

2.3. Button cell fabrication

Symmetrical button cells ($\sim 1 \text{ mm}$ thick, active area 0.64 cm^2) were

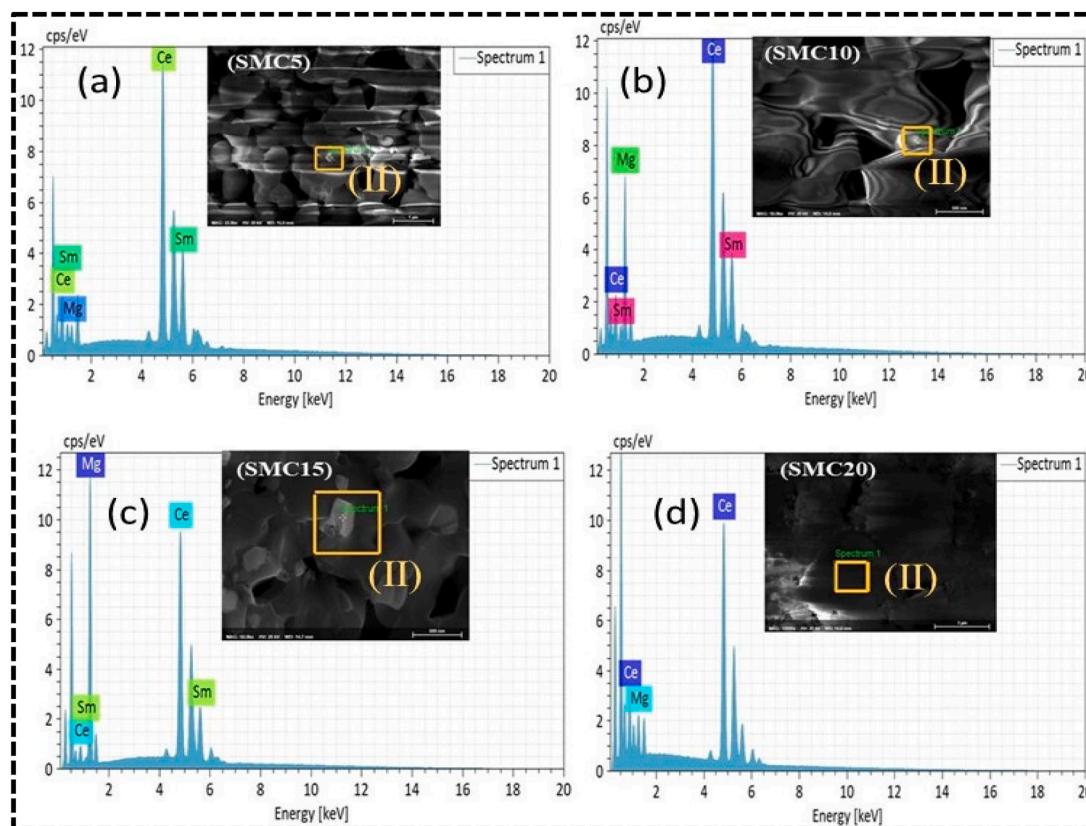


Fig. 6. EDS of SMC5–SMC20 samples annealed at 1200 °C with (II) showing traces of MgCO_3 related phase (a) SMC5 (b) SMC10 (c) SMC15 (d) SMC20.

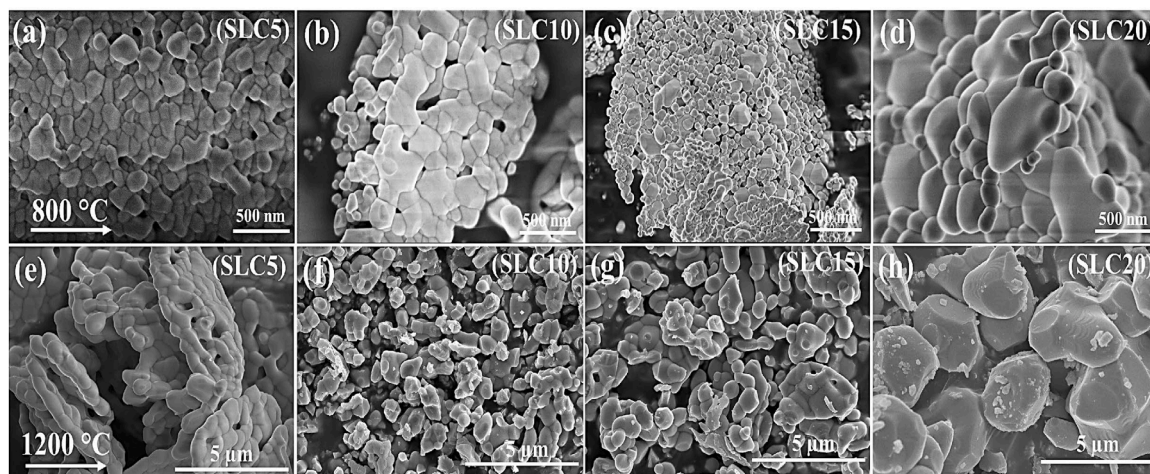


Fig. 7. Microstructures of SLC samples (SLC5–SLC20) annealed at 800 °C (a–d) and 1200 °C (e–h), respectively.

prepared by sandwiching selected samples (SMC5 and SLC5 annealed at 1200 °C) between $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_{2-\delta}$ (NCAL, commercially purchased) electrodes in a 13 mm die and applying 250 MPa. The fabricated button cells were sintered at 800 °C for 2 h and silver paste was coated on either side for current collection. A dc electronic load instrument (ITECH8511, ITECH Electrical Co., Ltd.) was used to record the I–V and I–P curves (between 500–600 °C) while constantly supplying H_2 (120 mL min^{-1}) as fuel at the anode and air (100 mL min^{-1}) as oxidant at the cathode.

3. Results and discussions

3.1. PXRD

Fig. 1 (a–c) and (d, e) depict the room temperature XRD patterns of SMC and SLC powders annealed at different temperatures. A face-centred cubic (fcc) ceria phase (space group $\text{Fm}\bar{3}\text{m}$; ICSD # 00-034-0394) [23] was witnessed for all samples at all annealing temperatures. The absence of carbonate related peaks for SMC samples suggests its presence is most likely as an amorphous form. For SLC5–SLC20 annealed at 800 °C, a very minor peak can be seen at 42.79° which was ascribed to a carbonate phase (ICSD # 069,133) [23],

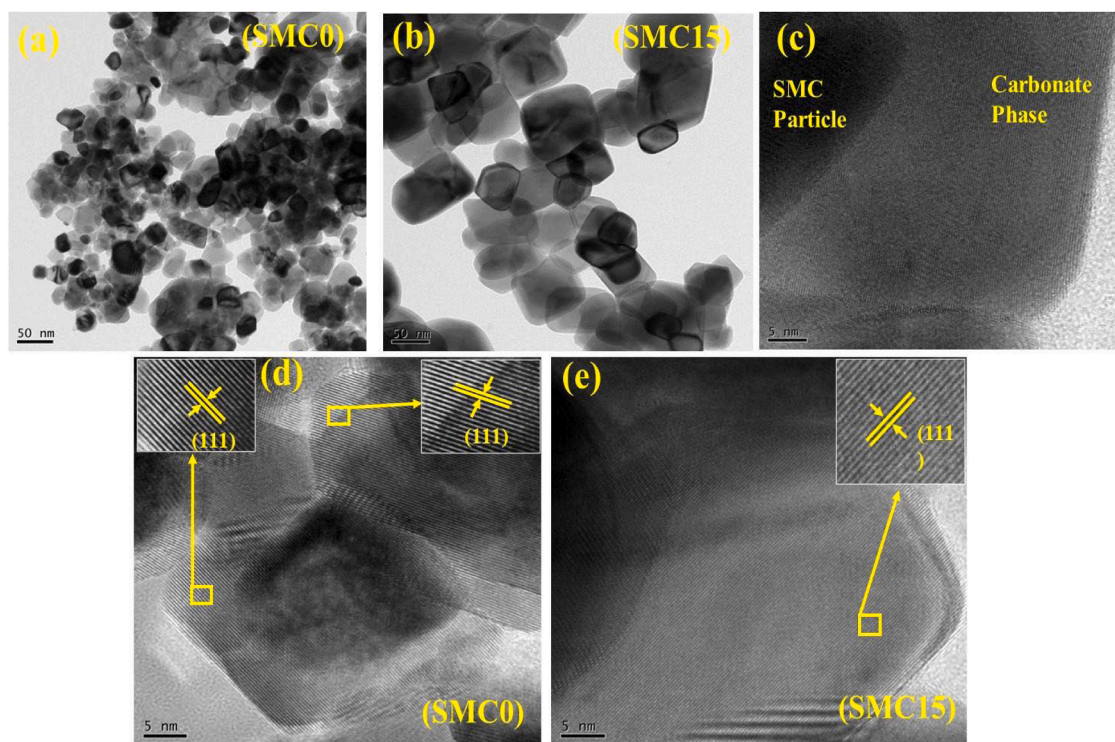


Fig. 8. HRTEM images of (a) SMC0 and (b,c) SMC15 annealed at 600 °C. (d, e) The high-resolution lattice fringes of SMC0 and SMC15, respectively.

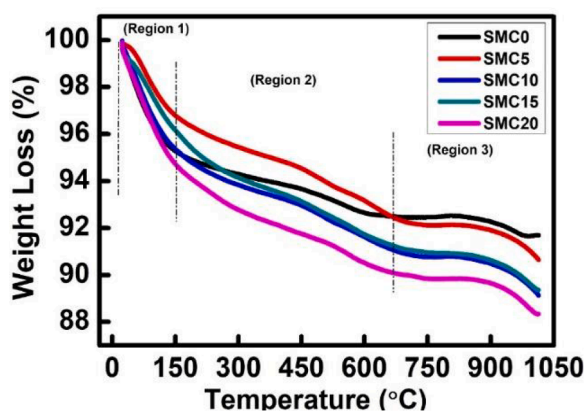


Fig. 9. TGA curves of SMC powders (SMC0–SMC20) already calcined at 400 °C for 4 h.

although as before, the carbonate phase is probably mainly amorphous. When annealed at 1200 °C, the minor peak (42.79°) disappeared due to expected volatilization of carbonate. In all cases it is unclear from XRD data whether Mg^{2+} or Li^+ carbonates form together with Na_2CO_3 . Based on Raman results, however, it was concluded that the peak at 42.79° was due to lithium carbonate indicating poor or incomplete incorporation of Li^+ content into the ceria lattice. On increasing the annealing temperature, peak widths decreased and intensities increased indicating improved crystallinity of all samples.

Given the ionic radii in decreasing order: Sm^{3+} (1.097 Å [24]) > Ce^{4+} (0.97 Å [22]) > Li^+ (0.92 Å [6]) > Mg^{2+} (0.72 Å [24]), it is expected that an increase in Mg^{2+} or Li^+ concentration coupled with a simultaneous decrease in Sm^{3+} content would result in a smaller unit cell parameter compared to that for 20 % Sm^{3+} doped ceria ($a = \sim 5.43$ Å [12]). A smaller value of a , however, does not imply that the Mg^{2+} or Li^+ is necessarily incorporated in the ceria lattice. Table 1 summarizes the relationship between dopant concentration and unit cell parameters

for SMC and SLC powders, where $a = \lambda \sqrt{(h^2 + k^2 + l^2)} / 2 \sin \theta$ [25], and theoretical densities determined from these are presented in Table S1. As expected, SMC0 and SLC0 have values of $a = \sim 5.43$ Å, except for the SMC0 sample annealed at 600 °C which has a value somewhat lower than expected, but still lies in the range 5.42–5.441 Å as described by Okay et al [26]. In general, the cell parameters of SMC powders annealed at 600 °C were lower than those of samples annealed at higher temperatures. This may indicate incomplete incorporation of metal ions into the ceria lattice at this stage, particularly Sm^{3+} as this discrepancy was not seen for SMC20 which did not contain Sm^{3+} . This may also be affected by the lower reliability in the lattice parameters obtained from broader peaks. No significant difference was observed in the unit cell parameters for the 800 °C and 1200 °C annealed samples, except for SLC20 where it dropped by ~ 0.01 Å on annealing at 1200 °C which could indicate a second stage partial incorporation of Li^+ into the ceria lattice. The SMC20 and SLC20 samples all gave values of a slightly less than that for pure ceria ($a = 5.411$ Å [23]) suggesting that only a small amount of Mg^{2+} or Li^+ was incorporated.

3.2. Raman spectroscopy

Fig. 2 (a–f) shows the room temperature Raman spectra of SMC and SLC powders annealed at different temperatures, with data also collected for the SMC series annealed at 400 °C. The variations in the F_{2g} band positions with respect to change in concentrations of dopants and annealing temperature have been summarized in Table 2. A general shift to higher wavenumber was noted when systematically decreasing the Sm^{3+} content and simultaneously increasing the amount of Mg^{2+} or Li^+ added. This shift in F_{2g} band position is attributed to the combined effect of the extent of impurity intrusion into the ceria lattice and the nanometric size of ceria particles [6]. The F_{2g} band for pure ceria has previously been reported at 462 cm^{-1} [18] and 465 cm^{-1} [27], thus it appears that the sequential removal of Sm^{3+} leads to the band moving closer to the position for ceria and hence the question arises as to whether Mg^{2+} or Li^+ are incorporated into the lattice. It was also

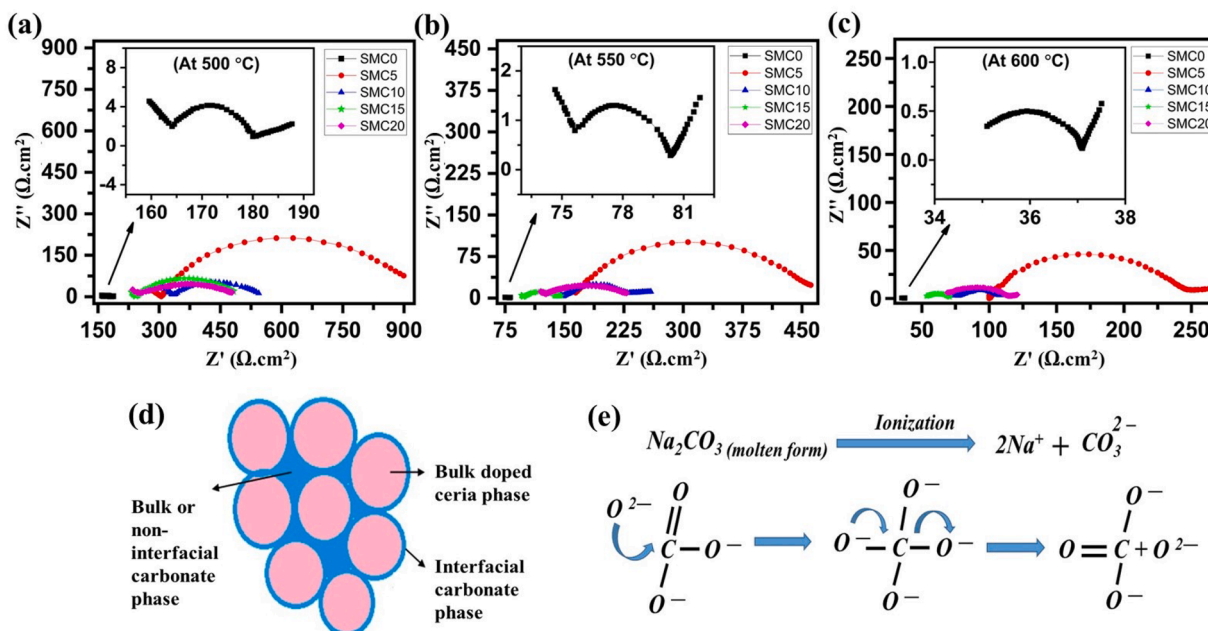


Fig. 10. Impedance spectra of SMC samples (SMC0–SMC20) annealed at 600 °C and measured over the temperature range 500–600 °C (a) 500 °C (b) 550 °C, and (c) 600 °C. (d) A hypothetical representation of the non-interfacial and interfacial phases of carbonate surrounding the ceria particles. (e) The proposed mechanism of oxide ion transport through molten carbonate.

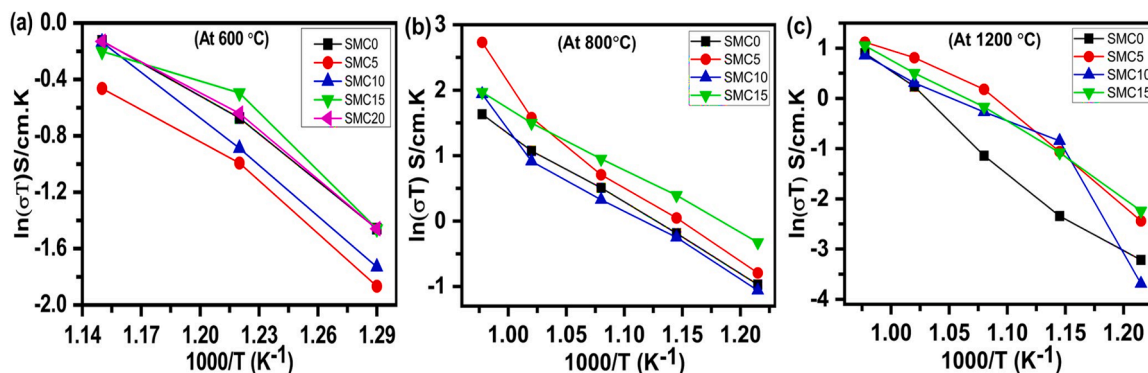


Fig. 11. Arrhenius plots of SMC samples annealed at (a) 600 °C (b) 800 °C and (c) 1200 °C.

observed that increasing the annealing temperature resulted in a shift to higher wavenumbers for each sample, probably due to an increase in grain size as expected for the higher temperatures, but a variation in the extent of dopant incorporation could also play a role.

To this end the oxygen vacancy bands at $\sim 550 \text{ cm}^{-1}$ and $\sim 600 \text{ cm}^{-1}$ were considered. The intensity of these bands systematically decreases when reducing the Sm^{3+} content with simultaneous increase in added Mg^{2+} or Li^+ . There were very small to undetectable oxygen vacancy bands for SMC20 and SLC20 materials. The quantitative analysis of the Raman spectra was performed using a Gaussian amplitude function to fit the peaks represented in Fig. 3 for SMC (and S1 for SLC) materials. The defect concentration was estimated as the area ratio of the oxygen vacancy band at $\sim 550 \text{ cm}^{-1}$ and the F_{2g} band ($A_{\sim 550}/A_{\text{F}_{2g}}$) [19], and the results are given in Table 3, which reiterate the trend seen for the oxygen vacancy bands. It can thus be concluded that the oxygen vacancies seem to be mainly generated by the incorporation of Sm^{3+} into the ceria lattice, indicating that Mg^{2+} or Li^+ was only doped into the lattice to a very small extent. Had Mg^{2+} or Li^+ occupied the vacated Sm^{3+} sites, it would be expected the oxygen vacancies would increase due to the lower charge on these ions. For SMC0 and SMC5 (samples with high Sm^{3+} content) annealed at 600 °C, the lower defect concentration indicates

that Sm^{3+} is not fully incorporated into the lattice, commensurate with the lower lattice parameters detected by XRD. Upon annealing to 800 °C there appeared to be further dopant incorporation, with no significant change when further annealed at 1200 °C. An increase in defect concentration was noted for all SMC samples on increasing the annealing temperature from 800 °C to 1200 °C, indicating a second stage partial incorporation of Li^+ , as was also signified by a decreasing lattice parameter from the XRD data, particularly for SMC20. On the other hand, SMC10–SMC20 showed a decrease in defect concentration with increasing annealing temperature suggesting the separation of Mg^{2+} in the form of a MgCO_3 related phase, particularly visible for SMC20 due to appearance of band at $\sim 1103 \text{ cm}^{-1}$ [28]. This may be because Mg^{2+} has a stronger affinity for CO_3^{2-} due to the electronegativity difference between CO_3^{2-} and host ceria.

The full width at half maximum (FWHM) of the F_{2g} band and the integrated area of the oxygen vacancy band at $\sim 550 \text{ cm}^{-1}$ (% relative intensity) were also obtained from the Gaussian amplitude function. These are presented in Tables S2 and S3, respectively.

In the higher absorption region ($1000\text{--}1800 \text{ cm}^{-1}$), bands represent the presence of carbonates, nitrates and overtones. In Fig. 2(b), SMC0 and SMC5 show a doublet at ~ 1079 and $\sim 1064 \text{ cm}^{-1}$ in agreement with

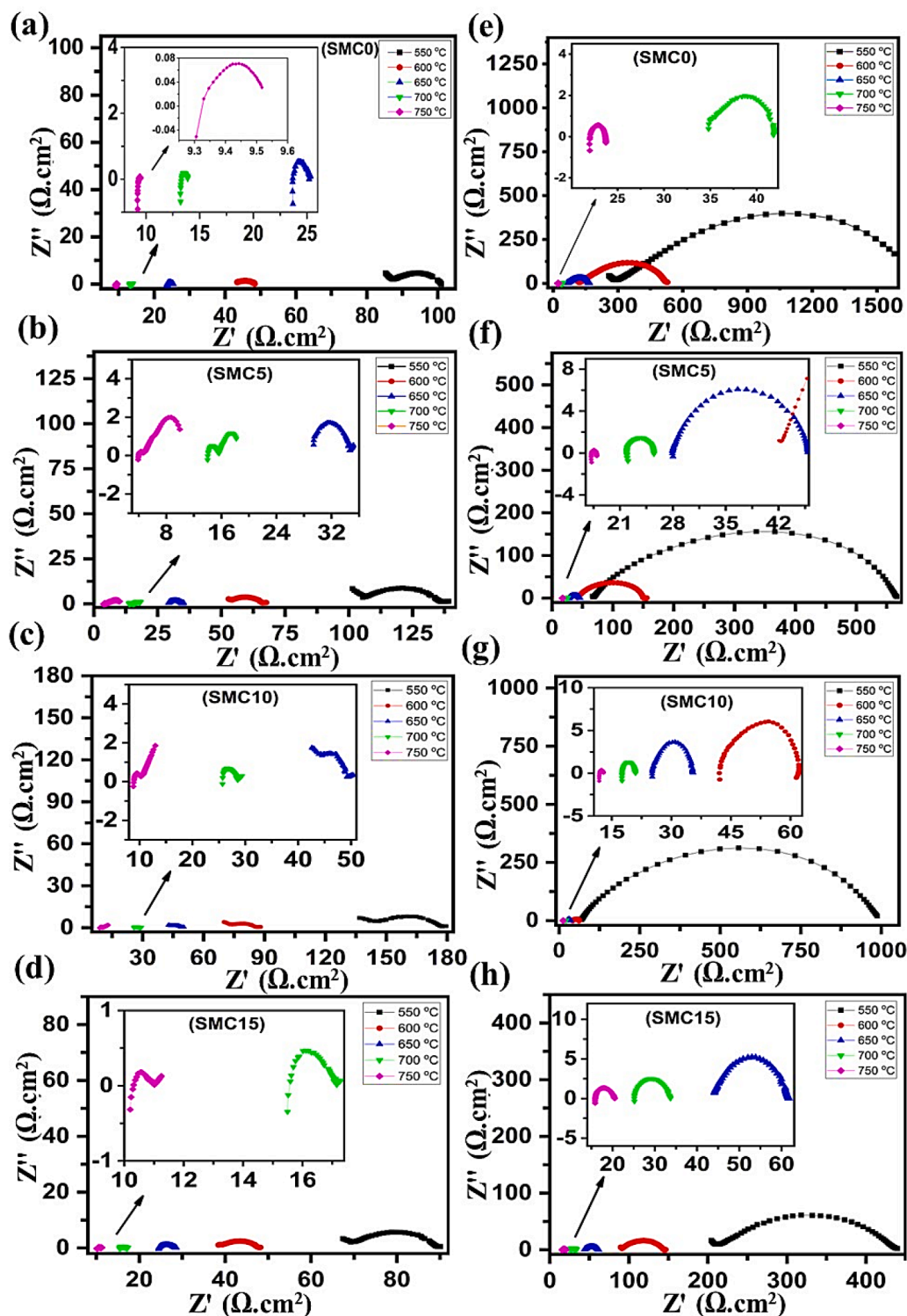


Fig. 12. Nyquist plots of SMC samples (SMC0–SMC15) annealed at 800 °C (a–d) and 1200 °C (e–h), recorded over 550–750 °C.

the earlier study on SDC/ Na_2CO_3 nanocomposite which represented the non-interfacial and interfacial phases of carbonate, respectively [29]. The higher the intensity of $\sim 1064 \text{ cm}^{-1}$ peak, the greater the strength of the interfacial phase which, in turn, may lead to enhanced interfacial conductivity [29]. SMC10–SMC20 only showed a single peak at $\sim 1079 \text{ cm}^{-1}$. By increasing the annealing temperature to 800 °C (Fig. 2(c)), slight variations were observed in the ν_1 region (~ 1000 – 1100 cm^{-1}), particularly for the sample with no Sm^{3+} content (SMC20). An expected effect of high temperature annealing is the volatilisation of excess

carbonate, i.e. the disappearance of the non-interfacial phase. For SMC0, only a single peak representing the interfacial phase was observed, which is downshifted ($\sim 1060 \text{ cm}^{-1}$) [19]. This down-shifting might be due to the stress caused by the high temperature on the interfacial phase to surround the ceria phase more tightly [19]. For SMC5, the doublet is again seen with a minor peak at $\sim 1060 \text{ cm}^{-1}$ and a comparatively intense peak at $\sim 1079 \text{ cm}^{-1}$ (similar to that for SMC10 and SMC15 annealed at 600 °C) which may indicate the presence of different carbonates, with $\sim 1060 \text{ cm}^{-1}$ to interfacial Na_2CO_3 and ~ 1079 to MgCO_3

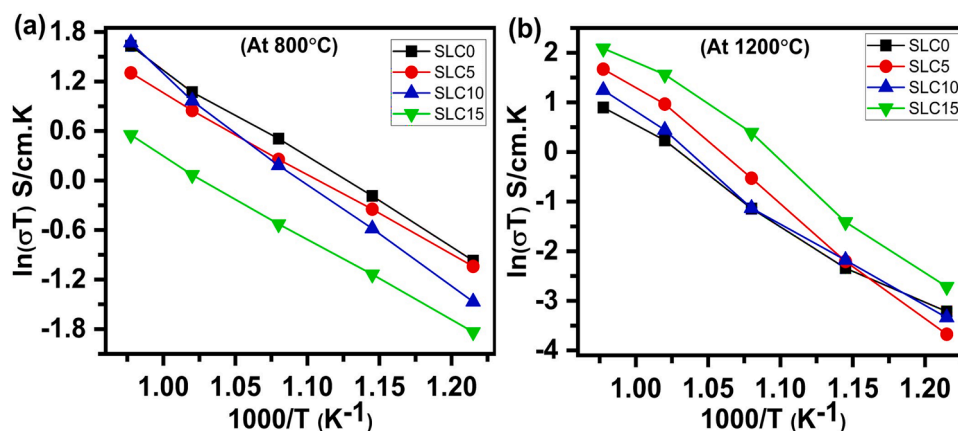


Fig. 13. AC conductivities of SLC samples (SLC0–SLC15) annealed at (a) 800 °C and (b) 1200 °C, measured from 550–750 °C.

related phase. SMC10 and SMC15 only show a very small carbonate peak at ~ 1079 cm⁻¹ (none at ~ 1060 cm⁻¹). The SLC sample displayed similar behaviour with a band at 1067 cm⁻¹ for SLC0, which is down shifted to 1060 cm⁻¹ for SLC5–SLC15 (Fig. 2(e)). For SLC20, a peak is visible at ~ 1087 cm⁻¹ which is reasonably close to 1091 cm⁻¹ for Li₂CO₃ reported elsewhere [30]. Interestingly, SLC5–SLC15 did not show the characteristic Li₂CO₃ peak even though evidence for this was seen in the XRD data (Fig. 1(b)). This might be because the peaks of both carbonates combine to appear as one. For all the 1200 °C annealed samples, the expected disappearance of CO₃²⁻ related bands are witnessed (Fig. 2 (d,f)). The ~ 1170 cm⁻¹ band has been assigned to 2LO mode of ceria (Fig. 2(d)) [31].

Interestingly, three bands positioned at ~ 1240 cm⁻¹, ~ 1315 cm⁻¹ and ~ 1360 cm⁻¹ can be seen for SMC0–SMC15, but are absent for SMC20 – the sample with no Sm³⁺ content. The same bands, slightly down shifted, for SLC0–SLC15 were observed (also absent for SLC20). Previously, Soni *et al.* observed these bands for CeO₂ particles doped with Sm³⁺ cations and assigned them to 3LO mode of CeO₂ which becomes activated because of multiphonon relaxation by resonance Raman effect [31]. This work reveals that these bands appear due to Sm³⁺ photoluminescence (PL). PL measurements were performed on the SMC powders annealed at 1200 °C and the bands subtracted from the Raman spectra to produce the spectra in Fig. 2(d) resulting in the absence of the three peaks at high wave numbers. The increase in intensities of these bands from SMC0–SMC15 might be suggestive of decreasing solubility of Sm³⁺ into ceria lattice as Sm³⁺ content was decreased.

The ν_2 region is generally Raman inactive, but under certain conditions, like local symmetry change or environmental effects, it may appear in the Raman spectrum. Bands at ~ 850 cm⁻¹ and ~ 950 cm⁻¹, were particularly obvious for SMC15 and SLC15 annealed at 800 °C (and 600 °C for SMC15). Previously, some authors have assigned these bands to peroxides on or close to ceria surface [32,33]. These bands, however, seem to be associated with the PL of Sm³⁺ as well. They are even visible for the 1200 °C annealed SLC15 (Fig. 2(f)) but are clearly absent for SMC15 after PL-related bands were subtracted (Fig. 2(d)).

3.3. FTIR

FTIR spectra of SMC and SLC powders annealed at different temperatures are shown in Fig. 4. Ceria is hygroscopic in nature, evident by the bands present for O–H stretching (~ 3435 – 3500 cm⁻¹) and H–O–H bending (~ 1620 – 1690 cm⁻¹) which is more pronounced for samples annealed at 600 and 800 °C. Two other bands which have widely been observed and reported in literature for ceria based materials are due to formate species (C–H stretching at ~ 2925 and ~ 2850 cm⁻¹), formed when ceria is exposed to the atmosphere [34,35]. The feature

below 700 cm⁻¹ represents the M–O vibrations [36,37].

For SMC powders annealed at 600 °C (Fig. 4(a)), the bands at ~ 1446 and ~ 1060 cm⁻¹ represent the antisymmetric and symmetric stretching of carbonate (ν_3 and ν_1 modes, respectively) matching well with those reported in literature [36,38]. Interestingly, as the Mg²⁺ content increases to above 5 mol% for these samples, a very small peak begins to appear in the high absorption region at ~ 3695 cm⁻¹ and becomes prominent for SMC20. According to literature, a characteristic peak of MgCO₃ is found in the region 3500 – 3700 cm⁻¹ due to O–H vibration [28,39]. The increase in intensities of peaks at ~ 3695 as well as ~ 1446 cm⁻¹ indicate that Mg²⁺ increasingly crystallizes out in the carbonate form. Based on these observations it is logical to relate the ν_1 Raman bands of SM10–SMC20 (annealed 600 °C) to a combination of Na₂CO₃ and MgCO₃ as the peaks of these carbonates are unresolved. The ~ 879 cm⁻¹ band has been assigned to out-of-plane bending of carbonates in ν_2 mode [36].

A very sharp peak occurs at ~ 1384 cm⁻¹ which increases in intensity with increasing Mg²⁺ (or decreasing Sm³⁺ content). Previously, the band at 1380 and 1384 cm⁻¹ was assigned to the NO₃⁻ group by Winck *et al.* and Seo *et al.*, respectively [37,40]. Different mechanisms have been proposed in literature by which formation of nitrates may take place on the ceria surface [41], but the use of precursor nitrate salts and the sharp peaks more likely indicate that nitrate does not decompose completely at 600 °C. For SMC0 and SMC5, the band observed at ~ 832 cm⁻¹ can also be assigned to nitrates in ν_2 mode, as reported elsewhere [42].

After annealing to 800 °C, distinct changes were evident (Fig. 4(b)). The bands representing the presence of carbonates and nitrates in the ν_3 region lose their intensities and shift slightly in position. For SMC0, the band at ~ 1730 cm⁻¹ has been assigned to Na₂CO₃, in agreement with that reported elsewhere [36]. Compared to SMC0, for samples SMC5–SMC20, the band assigned to carbonates in ν_3 region becomes sharp and shifts to higher wavenumber for SMC5 followed by splitting for samples with higher Mg²⁺ content (SMC10–SMC20), indicating that the presence of Mg²⁺ leads to the stabilization of carbonate phase. The features observed in the region ~ 850 – ~ 950 cm⁻¹ represent the out-of-plane bending of CO₃²⁻ in ν_2 region. The band located at ~ 750 cm⁻¹ has been assigned to C–O in-plane bending mode in ν_4 region. The characteristic feature at ~ 3700 cm⁻¹ indicating the MgCO₃ related phase is only barely seen for SMC15 and SMC20 [39]. The band representing the presence of nitrates is no longer observed signifying their decomposition, but for the spectra of the 1200 °C annealed samples (Fig. 4(c)) a very weak band at ~ 1381 cm⁻¹ suggests there is still a minor quantity of nitrates present on ceria surface [37,40]. Otherwise, the spectra in Fig. 4(c) only show features expected (~ 3450 cm⁻¹ and ~ 1635 cm⁻¹) due to the interaction of ceria with the surrounding environment.

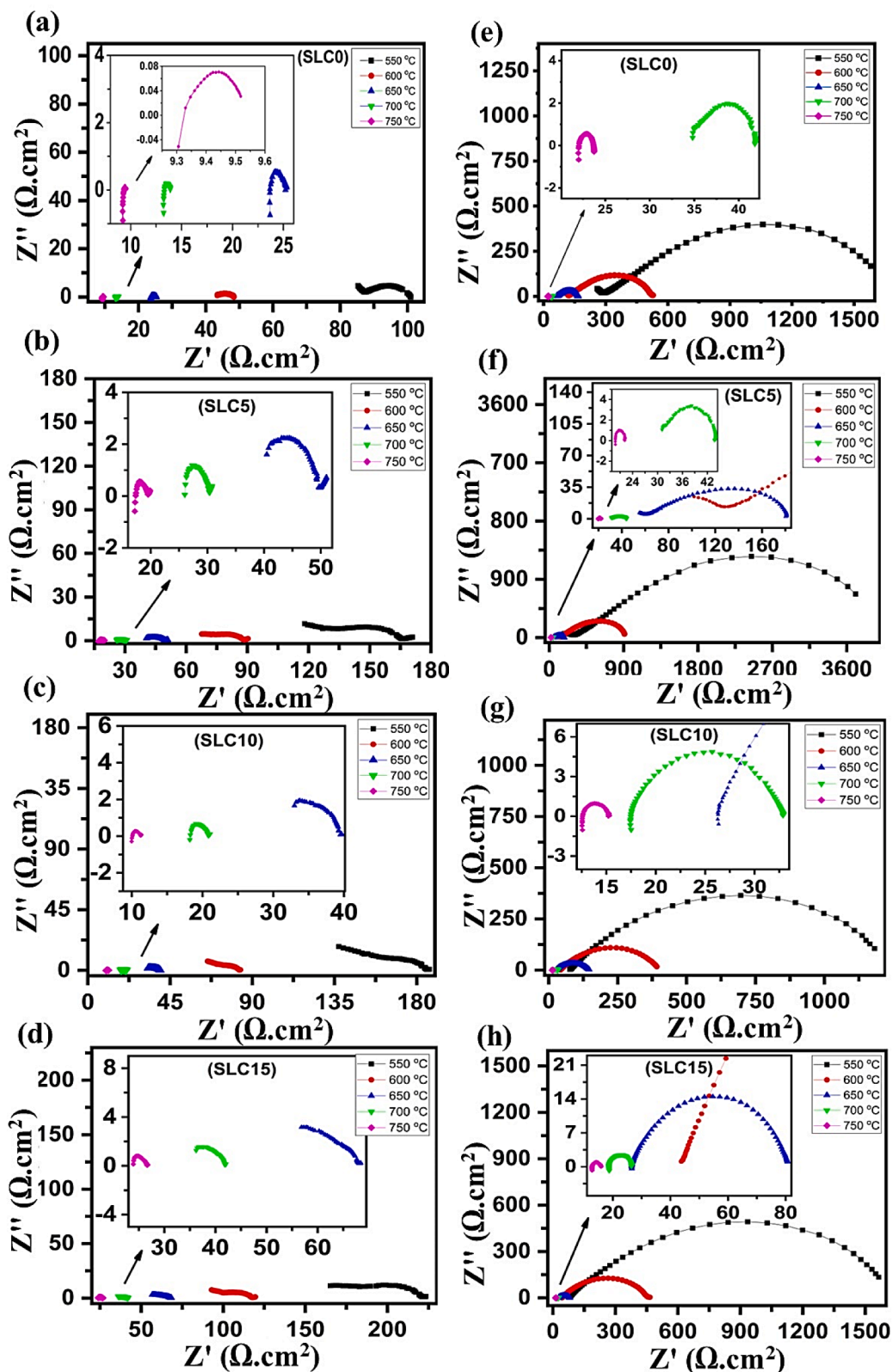


Fig. 14. Nyquist plots of SLC samples (SLC0–SLC15) annealed at 800 °C (a–d) and 1200 °C (e–h) measured over temperature range 550–750 °C.

The FTIR spectra of 800 °C annealed SLC powders (Fig. 4(d)) show the bands for moisture and the formate species, as well as the band corresponding to the asymmetric stretching mode of CO_3^{2-} at 1462 cm^{-1} , blue shifted compared to those for doped ceria at 1436 cm^{-1} and 1454 cm^{-1} reported by T. Ristoiu *et al.* and G. Accardo *et al.*, respectively [36,

38]. The weak band at 1060 cm^{-1} was also attributed to carbonates [37, 43]. The 1382 cm^{-1} band indicating nitrates [40] was only observed for SLC0. FTIR spectra of SLC powders annealed at 1200 °C were similar to those for the SMC powders (1200 °C annealed) and are not included here.

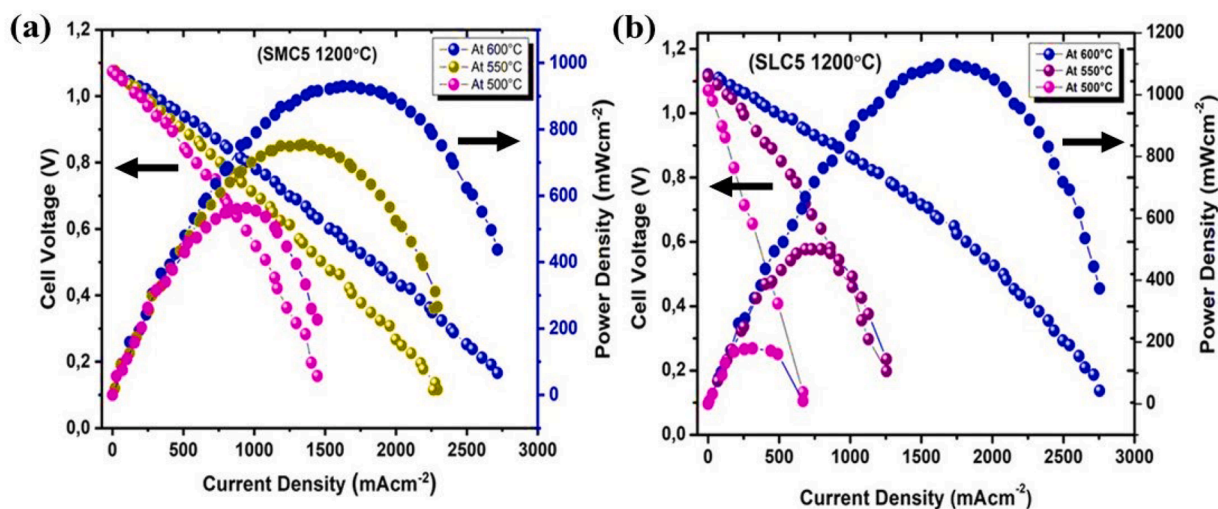


Fig. 15. I-V/I-P curves of button cells at 500–600 °C (a) SMC5 and (b) SLC5 electrolytes annealed at 1200 °C.

3.4. SEM

Fig. 5 shows the SEM micrographs for the SMC powders annealed at different temperatures. For 600 °C annealed powders (Fig. 5 (a–e)), nearly similar microstructure was observed for all samples with some degree of agglomeration due to presence of excessive carbonate (non-interfacial phase).

For 800 °C annealed samples (Fig. 5 (f–j)), an increment in particle size was observed with increase in temperature. An inhomogeneity was observed as Mg^{2+} was introduced. When annealed at 1200 °C (Fig. 5 (k–o)), particle inhomogeneity was also noticed, particularly with Mg^{2+} addition, along with particle growth, an expected effect of high temperature treatment. Slight agglomeration was seen for SMC10 and SMC15. For SMC20, particles with variety of shapes were seen.

EDS analysis performed for SMC5–SMC20 (1200 °C annealed samples) indicated the presence of Mg rich regions (Fig. 6). This further supports the results obtained by Raman spectroscopy and FTIR indicating the separation of at least some magnesium (most likely as the carbonate initially) rather than incorporation into ceria lattice.

Fig. 7 (a–e) shows the morphologies of (SLC5–SLC20) powders annealed at 800 °C which vary significantly with varying Li^+ concentrations. SLC0 and SMC0 are the same 20 mol% samarium doped ceria. With the introduction of 5 mol% Li^+ (SLC5) the particle morphology varies greatly resulting in particle elongation to form larger irregular shaped particles with some neck formation. According to Preethi et al [6], lithium enters the ceria lattice but tends to be at the grain boundary region. The crystallite growth occurs to minimize the surface energy, thereby causing neck formation.

Upon further addition of Li^+ (SLC10), the neck formation is further enhanced which indicates a decrease in surface energy. It is believed that during annealing, excessive amount of lithium tends to segregate at the grain boundary region. According to Preethi et al [6], this might be the result of the potential difference generated between lithium ions and space charge layer (positively charged grain boundary) upon lithium co-doping to generate oxygen vacancies. However, we believe that this segregation might be due to the presence of another species i.e., carbonate, having better affinity for Li^+ than Ce^{+4} to form lithium carbonate, leading towards a second phase, also detected by XRD, and strongly supported by Raman spectroscopy. In SLC15, particles of two different sizes can be seen, which might be representing two different phases. For SLC20, some smaller sized segregated particles can be seen which stay on the surface or fill the empty spaces between the bigger sized particles.

Clear particle growth can be seen after annealing at 1200 °C (Fig. 7

(f–j)). SLC5 seems to form a leaf or petal shaped structure, but still displaying the neck formation. SLC10 and SLC15 show more dispersed particles of irregular shape. SLC20 shows particles of considerably large sizes having circular shapes, quite different to that annealed at 800 °C.

3.5. TEM

Due to limited access to the instrument, high magnification TEM images were only obtained for selected samples. Fig. 8 shows the TEM images of SMC0 and SMC15 nanocomposites annealed at 600 °C. The carbonate phase is seen to coat the doped ceria particles (Fig. 8(c)). The composite can be rendered as a three-dimensional structure where particles are randomly packed [43]. Fig. 6 (d–e) shows the HRTEM images of these nanocomposites. The inter-planar spacing was found to be ~ 0.312 nm in both cases, which corresponds to the (111) plane, confirming the successful formation of crystalline ceria phase. The average grain sizes calculated from the TEM micrographs were 33 nm and 72 nm for SMC0 and SMC15, respectively.

3.6. TGA

Fig. 9 shows the TGA curves of SMC powders that had been calcined at 400 °C for 4 h. The TGA profile can be divided into three distinct regions. Region-1 (~ 25 – 150 °C) shows evaporation of physically adsorbed water. Region-2 (~ 150 – 700 °C) indicates the evolution of some species like NO_x , CO and CO_2 , along with the formation of a crystalline ceria phase [44–45]. In Region-3, carbonate in its molten form evaporates gradually, although more rapidly as the temperature goes beyond 900 °C. These TGA results allude to the reasonable stability of the SMC nanocomposite making them suitable for applications as SOFC electrolytes (provided compatible electrodes are used) capable of operation in the low temperature regime (600 °C or lower), but long term testing would need to be done [46].

3.7. EIS

The temperature dependent Nyquist plots of SMC and SLC powders annealed at 800 °C and 1200 °C were recorded in air from 550–750 °C (Fig.'s 10 and 12 for SMC, and Fig. 14 for SLC samples), and for the 600 °C annealed SMC samples the measurement temperature range was confined between 500–600 °C (Fig. 10 (a–c)). In general, the impedance spectra of the electrolyte materials comprise three distinct arcs corresponding to three different charge transport processes, i.e., bulk, grain boundary and electrode-electrolyte. The extent to which these arcs are

recorded is dependent on the various impedance values (which is also temperature dependant), especially with the instrument having an upper frequency limit of 1 MHz. The sum of the resistance of the bulk and grain boundary ($R_b + R_{gb}$), called the total conductivity (σ_t) here, were determined (Tables S4, S6) and used in the Arrhenius plots (Fig.'s 11 and 13). In all cases, a decrease in electrolyte resistance with increasing temperature is observed, as expected from thermally activated charge processes. The Nyquist plots for individual samples at each test temperature were plotted separately, fitted with suitable equivalent circuit based on observed data, and are presented in Fig.'s S2–S6.

For SMC powders annealed at 600 °C, the bulk resistance (in the high frequency region) may be associated with the bulk ceria and non-interfacial carbonate phases. The grain boundary refers to the region at the interface between the carbonate and ceria phases (intermediate frequency region), where the carbonate tightly surrounds the ceria particles. A hypothetical sketch representing interfacial and non-interfacial phases for doped ceria in the presence of the carbonate phase is depicted in Fig. 10(d). The carbonate phase conducts oxide ions according to the mechanism reported by Tong et al [15], as depicted in Fig. 10(e), which is analogous to the proton conductivity in water according to the Grotthuss mechanism [47].

From the Arrhenius plots (Fig. 11(a)), it is seen that for the co-doped samples (SMC5–SM15) as the Mg^{2+} content increases (and Sm^{3+} content decreases) there is an increase in conductivity. This correlates to the increase in defect concentration for these samples as obtained from Raman spectroscopy. Of particular importance is SMC20 (with no Sm^{3+} which gave the smallest defect concentration, but still indicated some Mg^{2+} intrusion into the ceria lattice) showing comparable conductivity to SMC0 (with no Mg^{2+} which gave the highest defect concentration), highlighting that both the effect of interfacial conductivity of carbonate and the partial intrusion of Mg^{2+} into the ceria lattice to generate oxygen vacancies at 600 °C play a role.

For the samples annealed at 800 °C (Fig. 11(b)), SMC20 showed considerably higher resistance, not suitable for electrolytic applications and thus not included here. No defect concentration was detected for this sample, thus showing that the carbonate phase alone is not responsible for oxide conduction. Although the order of conductivity for the remaining samples are different to that when the samples were annealed at 600 °C, the magnitude of the conductivities are similar at the measured temperatures of 550 and 600 °C. This is despite poorer incorporation of Mg^{2+} into the ceria lattice for the 800 °C annealed samples (especially for SMC10 and SMC15), once again highlighting the synergistic role of interfacial carbonate and the partial intrusion of Mg^{2+} into the ceria lattice. The Arrhenius plots for SMC5 and SM10 show an abrupt increase in conductivity between 700 and 750 °C which could be due to a second stage Mg^{2+} incorporation into the ceria lattice. SMC15 gave the highest conductivity at the lower temperatures, as well as the lowest activation energy (E_a) as determined from the slope of the Arrhenius plot (Table S5), compared to the other samples annealed at 800 °C which might be due to better interfacial conduction.

When annealed at 1200 °C, a decrease in conductivity was seen for all samples (especially SMC0) as compared to both the 600 °C and the 800 °C annealed samples (Fig. 11(c)). The grain boundary regions in the Nyquist plots of 800 °C annealed samples (Fig. 12 (a–d)) are flatter than those annealed at 1200 °C (Fig. 12 (e–h)), most likely due to the interfacial carbonate phase leading to reduced homogeneity and hence a more distributed effect. On average, an increase in activation energy is evident with an increase in the annealing temperature, pointing to the possible role of carbonate in reducing the activation energy.

Fig. 13 shows the Arrhenius plots for the SLC samples annealed at 800 °C and 1200 °C that were derived using the resistance values obtained from the Nyquist plots in Fig. 14. No noticeable response was seen for SLC20 due to extremely high resistance, despite there being a small defect concentration for the 800 °C annealed sample, the results are not shown. For the 800 °C annealed samples (Fig. 13(a)), it is seen that as more Li^+ is added (and Sm^{3+} content decreases) there is a general

decrease in conductivity. At 750 °C SLC10 has a comparable σ_t value to SLC0 due to the steeper slope.

Upon annealing at 1200 °C, there is almost a reversal in the trend with the sample with more Li^+ added (SMC15) giving the highest conductivity (Fig. 13(b)). At 550 °C, all samples showed considerably lower conductivity compared to the 800 °C annealed samples. At 750 °C, SLC10 and SLC15 showed increased conductivities compared to the 800 °C annealed samples, correlating to the increased defect concentrations noted from Raman spectroscopy data probably due to the incorporation of more Li^+ into the ceria lattice. Additionally at 750 °C, SLC0 and SLC5 showed slightly decreased conductivities compared to the 800 °C annealed samples, again correlating to the minimal change in defect concentrations upon further annealing.

As for the SMC samples, it was observed that semicircles representing the grain boundary are far flatter in Nyquist plots of 800 °C annealed samples compared to those annealed at 1200 °C (Fig. 14). The activation energies also increased with increase in the annealing temperature, thereby supporting the role of the carbonate phase noted before. Generally, the oxide conductivity was higher for the Mg^{2+} doped compared to the Li^+ doped samples annealed at 800 °C, and for the 1200 °C annealed samples the conductivity was slightly higher for the Li^+ doped compared to the Mg^{2+} doped samples.

3.8. Fuel cell performance

The I – V and I – P characteristics of fabricated button cells were measured over the 500–600 °C temperature range of using H_2 as fuel and air as oxidant and are depicted in Fig. 15. Both SMC5 and SLC5 (annealed at 1200 °C) exhibited good performance showing peak power densities (P_{max}) of 940 and 1120 mW/cm², respectively, which are considerably higher than 281.5 [48] and 630 mW/cm² [49] reported for SDC. An increase in P_{max} was observed with increase in temperature. Both cells showed impressive OCVs with values over 1.0 V at all operating temperatures suggesting negligible electronic conduction and suitability for practical applications, but the necessary stability studies still have to be done. Better performance was shown by SLC5 when the test temperature was raised to 600 °C probably due to second stage partial incorporation of Li^+ into ceria lattice.

4. Conclusions

This work focused on the preparation and investigation of co-doped ceria-carbonate based composite materials ($Ce_{0.8}Sm_{0.2-x}M_xO_{2.8}/\text{carbonate}$ where $M = Mg^{2+}, Li^+$) for electrolytic applications in LT-SOFCs. Although the beneficial role of carbonate in conductivity enhancement has been reported in literature, it was realized that the presence of carbonate may also have a negative effect on the incorporation of certain co-dopants into the host ceria lattice. Our studies suggest that carbonate combines with Mg^{2+} and Li^+ the supposed co-dopants used here, to form the respective carbonates due to the higher affinity of carbonates for these metal ions owing to the electronegativity difference between carbonate and host ceria. These carbonates ultimately get volatilized when annealed at 1200 °C resulting in loss of co-dopant metal ion, with some second stage incorporation for a few samples, particularly for SLC20. To exploit the beneficial trait of carbonate in conductivity enhancement, ceria-carbonate composite materials need to be annealed at lower temperature, preferably below 800 °C. However, a number of issues still need to be addressed such as incomplete incorporation of dopants into host ceria, and testing the compatibility of these composites with electrode materials.

Overall, better conductivity (combined bulk and grain boundary) was recorded for SMC samples annealed at 800 °C. This is most likely due to the role of carbonate since lower conductivities were found for the 1200 °C annealed samples where the interfacial carbonate phase was largely volatilised. It was noticed that the presence of carbonate resulted in lower activation energies for conduction. Although the formation of

respective co-dopant metal carbonate (MgCO_3 or Li_2CO_3) was noticed particularly from the Raman spectroscopy results, where the co-dopant intruded the ceria lattice, generation of oxygen vacancies was observed and noticeable effect on ionic conductivity was witnessed but only seen for SMC samples calcined at 600°C . It also appears that a significant role was played by Sm^{3+} in enabling the co-dopants to occupy the ceria lattice. For samples with no Sm^{3+} , the incorporation of the co-dopants (Mg^{2+} , Li^+) was found to be minimal. Hence, the incorporation of non-rare earth metals into rare earth metals needs further investigation, preferably using synchrotron-based techniques such as high resolution XRD and well as total X-ray scattering and X-ray absorption spectroscopy.

Supporting information

Theoretical densities of SMC and SLC samples, Multiple peak fitted Raman spectra of SLC samples, FWHM of F_{2g} bands of Raman spectra of SMC and SLC samples, Relative intensities of 550 cm^{-1} (relative to F_{2g}) bands measured from Raman spectra of SMC and SLC samples, Nyquist plots of SMC and SLC samples with equivalent circuits, total ionic conductivity values of SMC and SLC samples, Activation energies (E_a (eV)) of SMC and SLC samples.

The following files are available free of charge. Figures S1–S6, Tables S1–S6

CRediT authorship contribution statement

Muhammad Sarfraz Arshad: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Caren Billing:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition. **Wanbing Guan:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Naveed Mushtaq:** Software, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.surfin.2025.107776](https://doi.org/10.1016/j.surfin.2025.107776).

Data availability

Data will be made available on request.

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