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High performance ceramic nanocomposite fuel cells utilizing LiNiCuZn-oxide anode based on slurry method



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ABSTRACT

A multi-oxide material LiNiCuZn-oxide was prepared through a slurry method as an anode for ceramic nanocomposite fuel cell (CNFC). The CNFCs using this anode material, LSCF as cathode material and a composite electrolyte consisting of CaSm co-doped CeO₂ and (NaLiK)₂CO₃ produced ~1.03 W/cm² at 550 °C due to efficient reaction kinetics at the electrodes and high ionic transport in the nanocomposite electrolyte. The electrochemical impedance spectroscopy revealed low ionic transport losses (0.238 Ω cm²) and low polarization losses (0.124 Ω cm²) at the electrodes. The SEM measurements revealed the porous microstructures of the composite materials at electrode and the dense mixture of CaSm codoped CeO₂ and (NaLiK)₂CO₃. The Brunauer-Emmett-Teller (BET) analysis revealed high surface areas, 4.1 m²/g and 3.8 m²/g, of the anode and cathode respectively. This study provides a promising material for high performance CNFCs.

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Introduction

A ceramic nanocomposite fuel cell (CNFC) is an emerging fuel cell technology that utilizes materials from solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) technologies and operates at lower temperature (400° C-600 °C) [1–4]. The performance of the conventional SOFCs is limited below 650 °C due to low ionic conductivity of the electrolyte material, yttria-stabilized zirconia (YSZ) [5,6]. On the other hand, the degradation of the electrode materials at 650 °C is a serious issue for MCFC [7–9]. The CNFC overcomes these challenges by using the composite electrolyte with improved ionic

conductivity and the composite electrodes for device operation [10,11].

A variety of materials, lanthanum strontium manganite (LSM), lanthanum strontium cobaltite (LSC), lanthanum strontium ferrite (LSF), lanthanum strontium cobalt ferrite (LSCF), barium strontium cobalt ferrite (BSCF), lithiated NiO, etc, have been reported for cathode application of a CNFC [4,12–15]. Whereas, only fewer materials, NiO, LiNiZn-oxide, ZnO/NiO, are available for anode application [1,2,16–19]. The anode material is required to be an excellent catalyst for hydrogen oxidation reaction and resistant to any degradation. Nickel oxide and lithiated nickel oxide are the most commonly used catalyst materials for CNFCs. However, the

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nickel based anodes have low tolerance for H₂S containing fuels and degrade due to the formation of nickel sulphide and the physical adsorption of sulphur that blocks the reaction sites at anode [20,21]. Furthermore, these anodes are prone to coking when hydrocarbons and alcohols are used fuels, which can cause deactivation of reaction sites and even may lead to the mechanical damage. A copper based anode has been reported as a coking resistant material [22]. In another study, addition of La₂O₃ in NiO based anode improved the cell performance and stabilized the anode against NiO coarsening [23]. Similarly, copper oxide and zinc oxide have been reported to improve the performance of the nickel based electrodes [24,25] and also to decrease the solubility of nickel oxide in molten carbonate solution [26]. Therefore, a multi-oxide anode material is expected to improve the performance and stability of a CNFC.

In our previous study [27], we reported a LiNiCuZn-oxide as a potential electrode material for CNFC application and performed the material characterization. Symmetric cells were fabricated using this electrode material and electrochemical response was measured in air at 550 °C to study the oxygen reduction reaction (ORR). The performance of this potential electrode material at anode has not been studied yet and warrants a detail investigation as an anode material. Moreover, it is essential to study the performance under real fuel cell operation conditions (i.e. fuel at anode and oxidants at cathode).

In this work, a composite of LiNiCuZn-oxide with a ceriacarbonate electrolyte material is investigated as an anode material in the complete fuel cell devices. The CNFCs were fabricated using a nanocomposite electrolyte consisting of calciumsamarium co-doped cerium oxide and a eutectic mixture of sodium, lithium and potassium carbonate, prepared through a co-precipitation method. A composite of conventional LSCF was used as the cathode material. A detailed electrochemical analysis of the device is supplemented with comprehensive characterization of the materials (see Fig. 1).

Experimental section

Materials and fabrication

All the chemicals were purchased from Sigma Aldrich. The calcium and samarium co-doped ceria nanopowder was



Fig. 1 – Schematic structure of a ceramic nanocomposite fuel cell.

synthesized by a co-precipitation method. First, the materials Ce (NO₃)₃·6H₂O (35.92 g), Sm (NO₃)₃·6H₂O (9.19 g) and Ca $(NO_3)_2 \cdot 4H_2O$ (4.88 g) were dissolved in the de-ionized water. A 0.2 M solution of Na_2CO_3 (21.20 g Na_2CO_3 in 1000 ml in the deionized water) was dropwise added to the previous solution and stirred for half an hour, to give a white precipitation. This precipitate was filtered, washed and dried in the oven for 12 h at 80 °C. Afterwards, the mixture was sintered 800 °C for 4 h in air atmosphere. Afterwards, the powder was grounded in the mortar to give refined powder of calcium and samarium codoped ceria. In order to obtain co-doped ceria-carbonate nanocomposite electrolyte, Na2CO3, Li2CO3 and K2CO3 were mixed in their eutectic composition (Na2CO3: Li2CO3: $K_2\text{CO}_3=33.4\%$: 32.1%: 34.5%) and added to the co-doped ceria in a ratio of ceria: NLK-carbonate = 70: 30 wt%. The electrolyte mixture was milled for 1 h by the ball milling machine operating at 200 rpm and then ground for half an hour in a mortar. The pellets were made by pressing the nanocomposite electrolyte powder with a pressure of 250 MPa for 2 min in a 13 mm die. Afterwards the pellets were sintered at 690 °C for an hour. Finally, the gold paste was applied on both sides of the electrolyte pellets for current collection.

The nanoparticles of LiNiCuZn-oxide were synthesized by a slurry method. First, the materials including LiNO₃ (2.07 g), NiCO₃·2Ni(OH)₂·xH₂O (16.4 g), CuCO₃·Cu(OH)₂ (5.3 g), [ZnCO₃]₂·[Zn(OH)₂]₃ (8.4 g) and citric acid (10.5 g) were added in the deionized water and mixed with the help of a planetary ball milling machine for 1 h at 200 rpm. After mixing, the solution was simultaneously stirred and evaporated on a hotplate at 120 °C till a slurry-like mixture is formed. Afterwards, the slurry-like mixture was first heated in an oven at 400 °C for 1 and then calcined at 700 °C for 1 h to produce metal oxides. Finally, the mixture was milled for 1 h in a planetary ball milling machine operating at 200 rpm and then ground for half an hour in a mortar to get the nanopowder of LiNiCuZnoxide.

Composite anode and cathodes materials were prepared by mixing the LiNiCuZn-oxide and lanthanum strontium cobalt ferrite (LSCF) with the electrolyte powers, a binder and a pore former through solid route. The composition of the anode material was 50 wt% LiNiCuZn-oxide, 35 wt% electrolyte material, 7.5 wt% ethyl cellulose (EC) and 7.5 wt% polyvinyl alcohol (PVA). Similarly, the cathode material consists of 50 wt % LSCF, 35 wt% electrolyte material, 7.5 wt% of EC and 7.5 wt% PVA. The fuel cell pellets were made by placing the anode, electrolyte and cathode powders sequentially into a 13 mm die and pressed with a pressure of 250 MPa for 2 min. The pellets were sintered at 690 °C for an hour. Gold paste was applied on both sides of the fuel cell pellets to improve the electrical contact for fuel cell measurements.

Characterization

An XRD unit (PANalytical X'Pert PRO MPD, Rigaku Smarta) was used to measure the crystal structure of the materials. The measurements were conducted on the powder materials at room temperature using Cu K α_1 radiation (45 kV and 40 mA; $\lambda = 1.5406$ Å). Probostat electrochemical measurement station from NorECs Ltd. was used to perform the electrochemical measurements. The cells were sealed using a ceramic

adhesive material (Ceramabond 552, Aremco) to avoid any gas mixing between the outer and inner chamber of the probe. After the test arrangements were ready, the probostat was placed in a furnace and electrochemical measurements were performed using a Zahner Elektrik's IM6 impedance measurement unit.

The ionic conductivity of the nanocomposite electrolytes was measured using electrochemical impedance spectroscopy (EIS) in air for a temperature range from 250 °C to 700 °C. The EIS measurements were conducted at open-circuitvoltage (OCV) condition using an AC amplitude of 20 mV and a frequency range of 100 mHz to 100 kHz. The current densityvoltage (IV) and current density-power density measurements (IP) of the cells were performed at 450 °C, 500 °C and 550 °C in the presence of H₂ at anode and air + CO₂ at cathodes. The EIS measurements of the cells were performed at OCV at 550 °C in the presence of H_2 at anode and air + CO_2 at cathodes. The Brunauer-Emmett-Teller (BET) analysis (Micromeritics TriStar 3020) and scanning electron microscopy (SEM, Zeiss Sigma VP) were performed to measure the surface area of the porous electrodes, and the morphological properties of the nanocomposite electrolyte and the electrode, respectively.

Results and discussion

Characterization of nanocomposite electrolyte and electrode material

The crystal structures of the CaSm co-doped CeO₂ electrolyte and LiNiCuZn-oxide nanomaterials synthesized through the co-precipitation and slurry methods, respectively, were studied through XRD. The XRD measurement of CaSm codoped ceria powder revealed peaks at the $2\theta = 28.5$ (111), 33.0 (200), 47.4 (220), 56.3 (311), 59.0 (222), 69.3 (400), 76.6 (311) and 78.9 (420) as shown in Fig. 2a. These peaks were identified using the ICDD file No. 04-015-2396, which corresponds to doped cerium oxide. The XRD pattern of the LiNiCuZn-oxide powder is shown in Fig. 2b. The peaks at $2\theta = 37.25$ (111), 43.29 (200), 62.88 (220), 75.42 (311) and 79.4 (222), were identified using the ICDD file No. 04-006-8078, which corresponds to LiNiO. Similarly, the peaks at $2\theta = 35.58$ (002), 38.75 (200), 48.71 (-202), 51.43 (112), 53.62 (020), 58.26 (202), 61.69 (-113), 65.98 (022), 66.09 (-311), 72.24 (311) and 72.99 (221), were identified using the ICDD file No. 04-006-4185, which corresponds to LiCuO. The remaining peaks at $2\theta = 31.83$ (100), 34.48 (002), 36.32 (101), 47.63 (102), 56.71 (110), 62.97 (103), 68.09 (112), 69.23 (201) and 77.13 (202), were identified using the ICDD file No. 04-013-7260, which corresponds to LiZnO. The XRD pattern of CaSm co-doped ceria and LiNiCuZn-oxide thus confirmed the successful synthesis of these materials.

The SEM measurements were performed to study the morphology of the nanocomposite anode and electrolyte in the CNFC. Fig. 3a shows a porous network of composite nanomaterials at the anode. The average size of LiNiZn-oxide particles were found to be around 60 nm. In Fig. 2a, the size of the particles varies from up to 200 nm due to the formation of clusters. Fig. 3b shows a highly dense nanocomposite electrolyte. Both the co-doped ceria particles and the amorphous carbonate phase are visible in the image. The size of the oxide



Fig. 2 – Powder X-ray diffraction patterns of the (a) CaSm co-doped ceria, and (b) LiNiCuZn-oxide powders after sintering at 690 °C in air.

particles varies between 50 and 80 nm. The BET analysis revealed a high surface area $(4.1 \text{ m}^2/\text{g})$ of the anode. Since the electrochemical performance of the CNFC depends on the interfaces and the morphology of these composite materials, the porous structure of the composite electrode and the dense uniform mixture of the oxide and carbonate phases in the electrolyte, anticipate efficient reaction kinetics at the anode and high ionic conductivity of the nanocomposite electrolyte, respectively. The porous network of the electrode materials have been reported to facilitate the mass transfer which improved the reaction kinetics at the surface of the electrodes [28]. The dense electrolytes prevent gas crossover through the electrolyte layer and improved the interfaces between the doped ceria particles and the amorphous carbonate phase, which is crucial for the efficient ionic transport in the electrolyte layer [29,30].



Fig. 3 - SEM images of the nanocomposite (a) electrode and (b) electrolyte materials.

Table 1 – Values of ionic conductivity of the nanocomposite electrolyte from 250 °C to 700 °C. The Arrhenius plot of the ionic conductivity of nanocomposite electrolyte is shown in Fig. 4.													
Temperature (°C)	250	300	350	400	450	500	550	600	650	700			
Ionic conductivity (S/cm)	$6.9 imes10^{-6}$	$9.2 imes 10^{-6}$	$3.1 imes 10^{-5}$	0.05	0.16	0.20	0.24	0.28	0.30	0.32			

The ionic conductivity of the CaSm co-doped CeO₂ and $(NaLiK)_2CO_3$ nanocomposite electrolyte was measured at temperatures from 250 °C to 700 °C using EIS and the values obtained are presented in Table 1.

Fig. 4 shows the Arrhenius plot of its ionic conductivity, which consists of three distinct regions. In the first region, which consists of temperatures below 350 °C, the plot was quite linear in the natural logarithmic scale. In this region, the ionic conductivity was dominated by the conduction of oxygen ions through the bulk of the co-doped cerium oxide [3,31]. In the second region, which consists of temperatures between 350 °C and 450 °C, the ionic conductivity increased dramatically. This dramatic increase in the ionic conductivity around 400 °C was related to the melting of the alkali carbonates which enables alternative conduction channels for the ionic



Fig. 4 – Arrhenius plot of the ionic conductivity of the nanocomposite electrolyte measured through EIS.

transport in the electrolyte layer [1,2]. In the thrid region which is beyond 450 °C, the rate of increase in the ionic conductivity decreased and followed a linear curve in the natural logarithmic scale. This increase in ionic conductivity is related to the mobility of the charge carriers [1,2]. Fig. 4 shows the activation energy (23.9 kJ mol⁻¹) calculated from Arrhenius equation for the temperatures in this region, which is also the operating temperature of the CNFCs. Ionic conduction in these nanocomposite electrolytes is quite complex as they exhibit multipolar ionic conduction of native (Li^+ , Na^+ , K^+ , CO_3^{-2}) and foreign ions (O²⁻, OH⁻, H⁺) [32]. Transport of each of these ions contributse to the total ionic conductivity of the electrolyte. In order to study the contribution of the individual ion types, methods like electromotive force (EMF) [32] need to be applied to determine their ionic transport numbers. There are 4 different parallel channels for ionic transport in the electrolyte in this temperature region as suggested in the previous studies [3,31]: i) through the bulk of oxide phase, ii) through the bulk of molten carbonate phase, iii) through the interface between the oxide phase and the molten carbonate phase, iv) combination of channels (ii) and (iii). Most likely, the conduction channels (ii-iv) dominate the major ionic transport in the electrolyte layer.

For the sake of comparison we measured the ionic conductivity of the CaSm–CeO₂ electrolyte pellet, which gave a value of 0.038 S/cm at 550 °C, which is quite to the value reported in the literature 0.039 S/cm at 600 °C [33]. The ionic conductivity significantly increased to 0.24 S/cm with the addition of (NaLiK)₂CO₃ as shown in Table 1.

The ionic and electronic conductivity of LiNiCuZn-oxide was measured using EIS since these properties affect the catalytic properties of the electrode material. We found an ionic conductivity of 0.02 S/cm and an electronic conductivity of 9.83 S/cm at 550 °C. To improve the ionic conductivity of the electrode, a composite of the LiNiCuZn-oxide and nanocomposite electrolyte was used as the electrode material. In our previous studies on LiNiCuZn-oxide material we reported lower polarization losses in the cells prepared with the slurry



Fig. 5 – Cell voltage and power density versus current density under different operating conditions, H₂ at anode and air + CO₂ at cathode, at 450 °C, 500 °C and 550 °C.



Fig. 6 – a) EIS response of the cell measured at 550 °C using a frequency range of 100 mHz to 100 kHz, and b) An equivalent circuit model to fit the EIS response of the cell.

method (0.21 Ω cm²) as compared to the cells prepared with the solid state method (0.31 Ω cm²) [27]. Therefore, slurry method was chosen to prepare nanomaterials of the LiNiCuZn-oxide material in this study.

Table 2 – Values of resistances corresponding to fuel cell processes using the equivalent circuit shown in Fig. 6b.										
L1 (μΗ)	R_ electrolyte (Ω cm²)	R1 (Ω cm²)	R2 (Ω cm²)	R3 (Ω cm²)	$\begin{array}{c} \text{R_pol} \leq \\ \text{R1+R2+R3} \\ \text{(}\Omega \text{ cm}^2 \text{)} \end{array}$					
0.59	0.238	0.026	0.023	0.096	0.124					

Characterization of nanocomposite fuel cell

The CNFC was measured at different temperatures, 450 °C, 500 °C and 550 °C under fuel cell condition. The power densities of 0.26 W/cm², 0.56 W/cm² and 1.03 W/cm² were acheived at 450 °C, 500 °C and 550 °C, respectively as shown in Fig. 5. The cell exhibits an open-circuit voltages of 0.91, 1.02 and 1.14 V at 450 °C, 500 °C and 550 °C, respectively. The total resistance of the cell obtained through IV curve at maximum power point was 0.63 Ω cm². This high performance of the cells is a result of efficient ion transport in the electrolyte and reactions kinetics at the electrodes.

The EIS measurements were performed to further understand the impedance losses in the electrolyte and the electrodes of the cell. The EIS response of the cell is shown in Fig. 6a. The EIS curves were fitted to an equivalent circuit model shown in Fig. 6b, where Relectrolyte and L1 represent the ohmic resistance of the cell and the inductance of the measurement setup, respectively. The R1 and CPE1 represents the impedance due to the charge transfer reactions at the electrodes. The other two pair of R-CPE circuits represents the impedances due to the processes related to mass transfer at the electrodes and electrolyte/electrode interfaces. These parameters of the equivalent circuit model were used to fit the data and their values are shown in Table 2. Due to the long wire of the measurement setup, the inductance was very high (0.59 μ H). The ohmic resistance of the cell, which was mainly dominated by the resistance of the electrolyte, was 0.238 Ω cm². The efficient electrode processes were evident from the low charge transfer resistance (0.026 Ω cm²) and the low resistances (0.023 Ω cm² and 0.096 Ω cm²) due to masstransfer process in the cell. The polarization losses at the electrodes are approximately 0.124 Ω cm². Overall, the total cell resistance was 0.362 Ω cm² which is reasonably close the value (0.63 Ω cm²) obtained through IV measurement at maximum power point.

Conclusions

LiNiCuZn-oxide prepared through a slurry method is successfully demonstrated as a potential alternative material for CNFC application. Using this material, an excellent fuel cell performance of 1.03 W/cm² was achieved at 550 °C, which is quite close to the value 1.1 W/cm² previously reported using NiO based anode [1]. The polarization losses at the electrodes were low (0.124 Ω cm²) due to the effective reaction kinetics and mass transfer at the electrodes. The detailed microscopic analysis revealed a porous well connected network of particles at the electrode. The XRD analysis revealed the characteristic peaks of LiNiCuZn-oxide.

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REFERENCES

- Asghar MI, Heikkilä M, Lund PD. Advanced low-temperature ceramic nanocomposite fuel cells using ultra high ionic conductivity electrolytes synthesized through freeze-dried method and solid-route. Mater Today Energy 2017;5:338–46. https://doi.org/10.1016/j.mtener.2017.07.017.
- [2] Khan I, Asghar MI, Lund PD, Basu S. High conductive (LiNaK) 2CO3Ce0.85Sm0.15O2 electrolyte compositions for IT-SOFC applications. Int J Hydrogen Energy 2017;42:20904–9. https:// doi.org/10.1016/j.ijhydene.2017.05.152.
- [3] Asghar MI, Lund PD. Ceramic-carbonate nanocomposite fuel cells. Nanoworld 2016;3:7–11.
- [4] Asghar MI, Lepikko S, Patakangas J, Halme J, Lund PD. Comparative analysis of ceramic-carbonate nanocomposite fuel cells using composite GDC/NLC electrolyte with different perovskite structured cathode materials. Front Chem Sci Eng 2017:1–12. https://doi.org/10.1007/s11705-017-1642-2.
- [5] Wachsman ED, Lee KT. Lowering the temperature of solid oxide fuel cells. Science 2011;334:935–9. https://doi.org/ 10.1126/science.1204090.
- [6] Kakac S, Pramuanjaroenkij A, Zhou XY. A review of numerical modeling of solid oxide fuel cells. Int J Hydrogen Energy 2007;32:761–86.
- [7] Iacovangelo CD. Stability of molten carbonate fuel cell nickel anodes. J Electrochem Soc Solid State Sci Technol 1986;133:2410–6.
- [8] Ota K, Mitsushima S, Kato S, Asano S, Yoshitake H, Kamiya N. Solubilities of nickel oxide in molten carbonate. J Electrochem Soc 1992;139:667–71.
- [9] Doyon JD, Gilbert T, Davies G. NiO solubility in mixed alkali/ alkaline earth carbonates. J Electrochem Soc 1987;134:3035-8.
- [10] Zhu B. Advantages of intermediate temperature solid oxide fuel cells for tractionary applications. J Power Sources 2001;93:82-6. https://doi.org/10.1016/S0378-7753(00)00564-4.
- [11] Zhu B. Functional ceria–salt-composite materials for advanced ITSOFC applications. J Power Sources 2003;114:1–9. https://doi.org/10.1016/S0378-7753(02)00592-X.
- [12] Sun X, Li S, Liu X, Zhu B. Electrochemical performances of BSCF cathode materials for ceria-composite electrolyte low temperature solid oxide fuel cells. Int J Electrochem Sci 2007;2:462–8.
- [13] Xia C, Li Y, Tian Y, Liu Q, Wang Z, Jia L, et al. Intermediate temperature fuel cell with a doped ceria–carbonate composite electrolyte. J Power Sources 2010;195:3149–54. https://doi.org/10.1016/j.jpowsour.2009.11.104.
- [14] Mat MD, Liu X, Zhu Z, Zhu B. Development of cathodes for methanol and ethanol fuelled low temperature (300–600°C) solid oxide fuel cells. Int J Hydrogen Energy 2007;32:796–801. https://doi.org/10.1016/j.ijhydene.2006.12.012.
- [15] Leng Y, Chan SH, Liu Q. Development of LSCF–GDC composite cathodes for low-temperature solid oxide fuel cells with thin film GDC electrolyte. Int J Hydrogen Energy 2008;33:3808–17. https://doi.org/10.1016/j.ijhydene.2008. 04.034.
- [16] Huang J, Mao Z, Liu Z, Wang C. Development of novel lowtemperature SOFCs with co-ionic conducting SDC-carbonate composite electrolytes. Electrochem Commun 2007;9:2601–5. https://doi.org/10.1016/j.elecom.2007.07.036.
- [17] Di J, Chen M, Wang C, Zheng J, Fan L, Zhu B. Samarium doped ceria–(Li/Na) 2CO 3 composite electrolyte and its

electrochemical properties in low temperature solid oxide fuel cell. J Power Sources 2010;195:4695–9.

- [18] Zhao Y, Xiong D, Qin H, Gao F, Inui H, Zhu B. Nanocomposite electrode materials for low temperature solid oxide fuel cells using the ceria-carbonate composite electrolytes. Int J Hydrogen Energy 2012;37:19351–6.
- [19] Raza R, Liu Q, Nisar J, Wang X, Ma Y, Zhu B. ZnO/NiO nanocomposite electrodes for low-temperature solid oxide fuel cells. Electrochem Commun 2011;13:917–20.
- [20] Matsuzaki Y, Yasuda I. The poisoning effect of sulfurcontaining impurity gas on a SOFC anode: Part I. Dependence on temperature, time, and impurity concentration. Solid State Ion 2000;132:261–9. https://doi.org/10.1016/S0167-2738(00)00653-6.
- [21] Gong M, Liu X, Trembly J, Johnson C. Sulfur-tolerant anode materials for solid oxide fuel cell application. J Power Sources 2007;168:289–98. https://doi.org/10.1016/ j.jpowsour.2007.03.026.
- [22] Hanna J, Lee WY, Shi Y, Ghoniem AF. Fundamentals of electroand thermochemistry in the anode of solid-oxide fuel cells with hydrocarbon and syngas fuels. Prog Energy Combust Sci 2014;40:74–111. https://doi.org/10.1016/j.pecs.2013.10.001.
- [23] Yan A, Phongaksorn M, Nativel D, Croiset E. Lanthanum promoted NiO–SDC anode for low temperature solid oxide fuel cells fueled with methane. J Power Sources 2012;210:374–80. https://doi.org/10.1016/j.jpowsour.2011. 10.081.
- [24] Tan W, Fan L, Raza R, Khan MA, Zhu B. Studies of modified lithiated NiO cathode for low temperature solid oxide fuel cell with ceria-carbonate composite electrolyte. Int J Hydrogen Energy 2013;38:370–6.
- [25] Fan L, Zhu B, Chen M, Wang C, Raza R, Qin H, et al. High performance transition metal oxide composite cathode for low temperature solid oxide fuel cells. J Power Sources 2012;203:65–71.
- [26] Huang B, Li F, Yu Q, Chen G, Zhao B, Hu K. Study of NiO cathode modified by ZnO additive for MCFC. J Power Sources 2004;128:135–44. https://doi.org/10.1016/j.jpowsour.2003. 10.008.
- [27] Patakangas J, Jing Y, Asghar MI, Lund PD. Investigation of LiNiCuZn-oxide electrodes prepared by different methods: synthesis, characterization and properties for ceramic carbonate composite fuel cells. Int J Hydrogen Energy 2016;41:7609–13.
- [28] Chen Y, Lin Y, Zhang Y, Wang S, Su D, Yang Z, et al. Low temperature solid oxide fuel cells with hierarchically porous cathode nano-network. Nano Energy 2014;8:25–33. https:// doi.org/10.1016/j.nanoen.2014.05.010.
- [29] Khan MA, Raza R, Lima RB, Chaudhry MA, Ahmed E, Abbas G. Comparative study of the nano-composite electrolytes based on samaria-doped ceria for low temperature solid oxide fuel cells (LT-SOFCs). Int J Hydrogen Energy 2013;38:16524–31. https://doi.org/10.1016/j.ijhydene.2013.05.060.
- [30] Rafique A, Raza R, Akram N, Ullah MK, Ali A, Irshad M, et al. Significance enhancement in the conductivity of core shell nanocomposite electrolytes. RSC Adv 2015;5:86322–9. https://doi.org/10.1039/C5RA16763A.
- [31] Loureiro FJA, Rajesh S, Figueiredo FML, Marques FMB. Stability of metal oxides against Li/Na carbonates in composite electrolytes. RSC Adv 2014;4:59943–52.
- [32] Evans A, Xing W, Norby T. Electromotive force (emf) determination of transport numbers for native and foreign ions in molten alkali metal carbonates. J Electrochem Soc 2015;162:F1135–43.
- [33] Wang B, Wang Y, Fan L, Cai Y, Xia C, Liu Y, et al. Preparation and characterization of Sm and Ca co-doped ceria–La 0.6 Sr 0.4 Co 0.2 Fe 0.8 O 3–δ semiconductor–ionic composites for electrolyte-layer-free fuel cells. J Mater Chem A 2016;4:15426–36. https://doi.org/10.1039/C6TA05763B.