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Ionic conducting properties and fuel cell performance developed by band structures

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Abstract

The layer structure transition metal oxides have good triple $H^+/O^{2-}/e^-$ charge transport which can promote redox reactions and enhance fuel cell performance. This work has developed ionic transport property based on the layer structure $LiCoO_2$ (LCO) by tuning energy band structure with Mg doping also applied for the electrolyte in high-performance low-temperature solid oxide fuel cells (LT-SOFCs). Mg doped $LiCoO_2$ exhibited a hexagonal layered structure with $R3m$ space group. By doping the $LiCoO_2$ band gap was reduced from 2.65 eV to 2.24 eV. Electrochemical impedance analysis revealed Mg-doped LCO (LMCO) reducing significantly the polarization loss (charge transfer resistance) from 0.85 to 0.5 $\Omega\text{ cm}^2$ at 600 °C ; the power output of the fuel cell devices improved from 0.5 W/cm^2 to 0.7 W/cm^2 resulting also in better operation durability. Various characterizations on structural and electrochemical properties were conducted. The mechanism was further discussed relation with the band structures.

Key words: $LiCoO_2$, Mg doped $LiCoO_2$, Layered structure, Band structure, Fuel cell, Mixed ionic and electronic conduction.

1. Introduction

One of the critical hindrances in the state of the art SOFC's is the use of cathode materials that perform poorly at the electrochemical reduction of oxygen at low temperatures (LT) and

degrade over time under operating conditions.¹⁻² In addition, lack of ionic conducting electrolyte material is another critical issue on LT-SOFC R&D. In recent developments, the triple charge of $H^+/O^{2-}/e^-$ transportation in composite materials have demonstrated very successful LT-SOFC performances.³ In this context Co based mixed ionic-electronic conductors (MIEC's) like $SrCo_{0.7}Nb_{0.1}Fe_{0.2}O_{3-\delta}$,⁴ $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$,⁵ $Sm_{0.5}Sr_{0.5}CoO_3$,⁶ $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$,⁷ $BaCo_{0.7}Fe_{0.22}Y_{0.08}O_{3-\delta}$,⁸ and $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$,⁹ have been widely investigated because the Co produces low polarization resistance, as well as increasing both ionic and electronic conductivities in comparison with other SOFCs. All these materials were reported as quite good functional materials for LT-SOFC's with oxygen and proton ion conducting electrolytes. A summary on previously reported for the functional materials with mixed ionic (O^{2-}/H^+) – electronic (e^-) conducting properties offer promising performance for application in low-temperature solid oxide fuel cells (LT-SOFC). Recently, the family of lithiated transition metal oxides has attracted much attention to be used as promising functional materials with MIEC (mixed ionic and electronic conduction) property for LT-SOFC's. Layer structured $LiCo_{0.5}Al_{0.5}O_2$ (LCAO) has been already proven to have high proton conductivity, 0.1 S/cm at 500 °C, which was used as potential electrolyte in fuel cells and as a cathode material in Li-ion batteries as well as a proton conducting material upon Li^+/H^+ exchange reactions in fuel cell testing conditions in the presence of H_2 .^{10,11} However, the material has its own structural limitation i.e. the rhombohedral structure lead to collapse upon delithiation ($> 0.5Li$) ions, which reduces the cell cyclability, thereby, limiting the commercial applicability. On the other hand, a high amount of cobalt in LCO, generally, unstable at higher operating temperatures due to its large thermal co-efficient behavior and also increases basic material cost.¹² Alternatively, attempts were made to substitute some proportions of Co site with Ti, Zr, Mn, Mg etc.¹³⁻¹⁶ transition dopants in LCO layered structure. Recently, Zhu et.al,¹⁷ reported $LiNiFeO_2$ used as the semiconductor-ionic composites used for advanced LT-SOFCs, Zhang et.al,¹⁸ reported the use of $LiNi_{0.79}Co_{0.2}Zn_{0.01}O_2$ cathodes in SDC electrolyte based SOFC's and presented a peak power density up to 1.32 W/cm² at 650 °C with hydrogen as fuel. In his case, the improvement in the power densities was attributed to the use of partial substitution of Li^+ at Ni^{2+} sites introduces a hole in the form of Ni^{3+} or O^{2-} to keep the charge neutrality, thereby increasing its electrical conductivity. On the other hand, $LiNi_{0.79}Co_{0.2}Zn_{0.01}O_2$ introduces the extrinsic proton conduction pathways between two adjacent NiO layers forming a unique layered structure through lithium intercalation. Lan et al.¹⁰ have also reported higher proton conductivity using similarly layered oxide LCAO which suggested to substitute Co sites, maybe with the non-transition metals (Al, Ca and Mg) with fixed oxidation states. Tukamoto

et.al.¹⁹ reported that substitution of Mg^{2+} for Co^{3+} greatly enhanced the structural stability as well as the electronic conductivity of the pristine LiCoO_2 due to enlargement of inter-layer space (is called pillar effect) thus reduces the Li-ion transport resistance so that a significant mass of lithium ions are extracted from/into the host matrix. Based on our previous studies on RF magnetron sputter deposited pristine, Ti and Zr doped LiCoO_2 thin films as a cathode material in Li-ion batteries,^{20, 21} the present work are to extend LiCoO_2 application for SOFCs. It may be noticed that the layer structure materials exhibit excellent proton conduction, i.g. the best proton conductivity 0.1 S/cm at 500 °C demonstrated for LCAO in the interlayer spaces used as the electrolyte materials under the fuel cell condition.^{3,10}, the main scope of this study is to develop further the layer structured material advantages by doping to tune band structures and further constructing heterostructure materials with ionic conductors to enhance the ionic conduction.²²⁻²⁵ We have demonstrated the feasibility of changing semiconductor band structures by doping to readily make strong impact on the electrical properties and the overall device's electrochemical performance of the SOFC's. By doping to tune the band structure and material properties, we can also improve the durability of the LCO based membrane fuel cells.

2. Experimental

2.1 Sample preparation and Fuel cell fabrication

The pristine LiCoO_2 powders are prepared by Sol-Gel method: LiNO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ethylene glycol with a molar ratio of 1:1:2 were dissolved in deionised water. The entire process was carried out under continues stirring at 100 °C until fully removal of the solvent. Then the resulting sol was dried at 130 °C to get rid of the impregnated water and finally calcinated at 800 °C for 4 h to produce LiCoO_2 powder. The preparation process of $\text{LiMg}_{0.1}\text{Co}_{0.9}\text{O}_2$ powders is similar with that of LiCoO_2 . In order to incorporate the Mg, a required amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was deliberately added the precursory solution.

The $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$ powder is prepared by Sol-Gel method: $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with a molar ratio 0.8:0.2 were dissolved in deionised water. Then, the prepared Na_2CO_3 solution (metal to carbonate ratio of 1:2) was added as a precipitant under continuous stirring at 80 °C for 6h, thereafter the excess carbonate was removed by vacuum filtration and washed three times and dried in the oven at 120 °C overnight. The dried samples were ground and calcinated at 800 °C for 4 h to produce $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$.

The fuel cell was fabricated by dry pressing method. LCO-SDC and LMCO-SDC composite materials were sandwiched between two pieces of NCAL ($\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$) coated Ni foam, then pressed under 10 MPa to form the symmetrical configuration of Ni-NCAL/LCO-SDC/Ni-NCAL and Ni-NCAL/LMCO-SDC/Ni-NCAL. The active area and thickness of these cells is 0.64 cm^2 and 1.9 mm, respectively.

2.2 Physical characterization

The crystal structure of these prepared samples was studied by a Bruker D8 X-ray diffractometer (XRD, Germany, Bruker Corporation) with CuK_α radiation ($\lambda=1.5406\text{ \AA}$) in the diffraction angle (2θ) range $10^\circ - 90^\circ$ with a scan speed of 0.03 degree/sec . The peak positions were determined precisely using the RAYFLEX-Analyze software. The morphologies of samples were investigated by field emission scanning electron microscope (FE-SEM, JEOL, JSM7100F) equipped with an energy dispersive spectrometer (EDS). To further characterize the microstructure, ultra high resolution transmission electron microscope (HR-TEM) was performed using a FEI Tecnai G2 F30 field-emission microscope operating under an accelerating voltage 300KV. X-ray photoelectron spectroscopic (XPS) studies were performed to analyze the oxidation state of the chemical composition using VG Multilab-2000 with Al $\text{K}\alpha$ anode (1486.6 eV) in ultrahigh vacuum ($5\times 10^{-10}\text{ mbar}$).

2.3 Optical and Electrochemical characterization

The optical reflectance study was carried out with a UV-Vis-IR spectrometer (Model: SHIMADZU 3600) in the wavelength range 300-2500 nm at room temperature. The electrochemical characterization of fuel cells was carried out by a computerized instrument (IT8511+, Ed, electronics co., LTD). Here the hydrogen was used as fuel and air as an oxidant with a flow rate of $80\text{-}90\text{ ml min}^{-1}$ and $120\text{-}150\text{ ml min}^{-1}$ under 1 atm, respectively. Electrochemical impedance spectrum (EIS) analysis was conducted by an electrochemical workstation (CHI-660D) under open circuit voltage with a 10 mV AC signal over the frequency range of $0.1\text{-}10^5\text{ Hz}$.

3. Results and discussion

3.1 Microstructural Properties

The XRD patterns of SDC, LCO, LMCO, LCO-SDC and LMCO-SDC powders sintered at 800 °C for 4h are shown in Fig. 1. The characteristic diffraction peaks of LCO and LMCO can be indexed as a layered structure based on a hexagonal α -NaFeO₂ structure with R3m space group and no appreciable impurity peaks were observed for the Mg-doped LCO sample, these results are well matched with the standard JCPDS data (Card number: 750532). LMCO reveals well split characteristic peaks (0 0 6)/(0 1 2) and (1 0 8)/(1 1 0) in comparison with LCO, which indicates that there is a dimensionally stable structure with a highly ordered array of Co and O₂ atoms in the layered structure. From XRD results, LCO and LMCO hexagonal lattice parameters obtained are: $a = 2.812$, $c = 14.031$ ($c/a = 4.98$) and $a = 2.819$, $c = 14.090$ ($c/a = 4.99$) respectively; the slight increase of LMCO lattice constants and c/a ratio in comparison with LCO is attributed to the bigger ionic radii of $r(\text{Mg}^{2+})$ ($= 0.72 \text{ \AA}$) than the ionic radii of $r(\text{Co}^{3+})$ ($= 0.525 \text{ \AA}$), therefore Mg^{2+} is incorporating into Co and the LiCoO₂ layer should mainly increase the inter-slab spacing of the layered structure (Fig. 2),²⁶⁻²⁸ thus helping to facilitate the hasty intercalation of Li^+/H^+ and oxide ions into the hexagonal host matrix under fuel cell conditions. As a result these compounds are expected to possess higher ionic conductivity and better electrochemical performance after Mg doping. Moreover, the LCO-SDC and LMCO-SDC composite diffraction peaks indicate the co-existence of individual phases for LCO, LMCO, and SDC. No additional diffraction peaks and no distinct shift can be observed in the diffraction patterns, indicating that no other chemical phases were formed from interactions between the LCO, LMCO, and SDC. LMCO-SDC and LCO-SDC composite being yielded as chemically stable materials is critical for the stability of the assembled fuel cell device.

FE-SEM of the LCO, LMCO, SDC, LCO-SDC and LMCO-SDC powders sintered at 800 °C is given in Fig. 3. Fig. 3 (a) and (b) shows a well-crystallized hexagonal shape for both LCO and LMCO which can be seen without displaying agglomeration. The morphologies of LCO and LMCO look very similar, although the particle size (about 200 nm) of LMCO is smaller than that of LCO (about 300 nm). It is known that the small particles can have a large surface active area with better contact of the electrode and electrolyte composite.²⁹ Fig. 3 (c) shows the SDC electrolyte is dense except minor closed pores, and the LMCO-SDC composite displays good interconnectivity between particles, as well as showing a greater number of conductive

pathways being present when compared with LCO-SDC composite shown in Fig. 3 (d) and (e), and the average grain size is much smaller than $1\mu\text{m}$. Fig. 3 (f). shows the cross-sectional microstructure of the fuel cell consisting of a 1.2 mm dense LMCO-SDC composite material and 340-360 μm NCAL-coated Ni foam on both sides of the composite material and shows in-depth the resulting Ni-NCAL/LMCO-SDC/Ni-NCAL nanocomposite SOFC. Furthermore, TEM was utilized to characterize the microstructure of the LCO-SDC and LMCO-SDC composites. LMCO-SDC composite shows (Fig. 3 (h)) homogeneously distributed with good contact between the particles then LCO-SDC composite (Fig 3 (g)). This behaviour due to the effect of Mg doping dispersed in the composite, which constrain the accumulation of the composite material grains. Fig 3 (i) shows the well-defined lattice fringes, confirming the high crystallinity and the crystal size of the LMCO and SDC is very fine. As can be seen from Fig 3 (i), the measured crystal lattice fringes d-spacing of LMCO was approximately 0.23 nm which correspond to the (0 0 6) plane of hexagonal phase ($R3m$ space group) and 0.31 nm d-spacing is ascribed to the (1 1 1) plane of SDC, which shows a good agreement with the XRD results as shown in Fig. 1. As Figure S₁ in the supporting information shows, the EDS elemental mapping of LMCO-SDC composite material reveals the uniform distribution of Co, Mg, Ce, Sm, and O, indicating the formation of LMCO-SDC composite material; this kind of composite can offer the possibility of rapid oxygen and proton transport and sufficient active sites for ORR.

The presence of elements and their oxidation states in LCO-SDC and LMCO-SDC composite were further examined by XPS technique. The survey spectrum of composite fuel cells exhibited characteristic photoelectron emissions at binding energies (BEs) corresponding to Li, Mg, Co, Ce, Sm, C and O elements, shown in supporting information Figure S₂. Fig. 4 (a) and (b) shows the BE peak for Li 1s at 54 eV and Co 2p core peaks were detected as two parts, Co 2p_{3/2} and Co 2p_{1/2} at 779.4 and 794.7 eV BEs, respectively. This demonstrates that the oxidation state is Co³⁺ in the LCO-SDC composite material. The LMCO-SDC composite material exhibits the core peaks for Co (2p_{3/2} at 779.56 and 2p_{1/2} at 794.86 eV) slightly shifted to a higher binding energy than LCO-SDC composite material, indicating the possible partial oxidation of Co³⁺ to Co⁴⁺. The presence of Co³⁺ and Co⁴⁺ could facilitate the oxygen reduction and evolution reactions.^{30,31} Mg 1s BE peak detected at 1303.4 eV is assigned to the Mg²⁺ and it confirms the existence of Mg²⁺ in the LMCO-SDC composite material shown in Fig. 4 (c). The peaks in the spectrum of Ce 3d were observed in different ionic states such as Ce³⁺ (BEs are 3d_{5/2} at 878 and 3d_{3/2} at 896 eV) and Ce⁴⁺ (BEs are 3d_{5/2} at 898.3 and 3d_{3/2} at 916.6 eV) shown in Fig. 4 (d). Fig. 4 (e) shows the Sm 3d (3d_{5/2} at 1080.5 and 3d_{3/2} at 1107.4 eV) peaks

which confirm the doping of Sm in CeO₂ nanomaterial.³² The O 1s photoemission peaks display the BEs at 528.6 and 531 eV for all the composite cells, and observed the higher intensity for Mg-doped composite material than the Mg-free composite material, which means that a stronger interaction occurred between the composite catalysts and adsorbed oxygen-containing species due to the synergistic effect, which is an advantage for the process of oxygen reduction reactions shown in Fig. 4 (f). Hence, these XPS and EDS observations confirm the formation of LCO-SDC and LMCO-SDC composite materials.

3.2 Electrochemical properties and chemical stability

The impedance spectra were employed to understand the kinetics of ORR and electrocatalytic activity of the samples. The typical Nyquist plots of LCO-SDC, LMCO-SDC based cells from 500 °C to 600 °C in the air are shown in Fig. 5 (a) and (b), respectively. An equivalent circuit model of $LR_{ohm}(R_1Q_1)(R_2Q_2)$ presented as an inset in Fig. 5 (b) was used to fit the raw data by ZSimpWin software. L is caused by the inductance of the electrical equipment and electric wire and R_{ohm} is mainly due to the ohmic resistance of the entire cell. In addition, R_1/Q_1 and R_2/Q_2 represents the high frequency and low-frequency resistance/capacitance, respectively. The high-frequency arc involves charge transfer during the migration and diffusion of oxygen ions from electrode/MIEC's interface, and the low-frequency arc is ascribed to the non-charge transfer process, such as oxygen surface exchange and oxygen gas diffusion through the electrode.^{33,34} The impedance of LCO-SDC and LMCO-SDC are 5.1, 2.4 and 0.85 Ω cm² and 2.6, 1.03 and 0.5 Ω cm² at 500, 550 and 600 °C, respectively. Both cell resistances decrease noticeably with increasing temperature, indicative of thermal activation behaviour of the electrode reaction process. Particularly, the lower charge transfer resistance of LMCO-SDC based cell is attributed to the replacement of Co³⁺ ions by lower valence Mg²⁺ ions that through charge compensation leads to the generation of Co⁴⁺ (holes) ions ($2Co^{3+} \rightarrow Co^{4+} + Mg^{2+}$), thus enhancing the effective carrier concentrations whilst simultaneously reducing the area specific resistance (ASR) of Mg-doped LiCoO₂.

The electrical properties of LCO-SDC and LMCO-SDC composite fuel cells were studied based on EIS. From the EIS, the total electrical conductivity was calculated according to:

$$\sigma_t = \frac{L}{R_{ohm} \times A}$$

Where L denotes the thickness, A is the effective area of the fuel cell and R_{ohm} is ascribed to the ohmic resistance that was contributed by both ions and electrons. Meanwhile, the ionic

conductivity (σ_i) of both LCO-SDC and LMCO-SDC composite cells can be estimated from the slope of I-V curves (Fig. 7) according to:

$$\sigma_i = \frac{L}{R_{ASR} \times A} = \frac{L \times i}{V_{ohm} \times A}$$

Consequently, the electronic conductivity (σ_e) can be obtained from the σ_i , according to $\sigma_e = \sigma_t - \sigma_i$. At different temperature, the obtained conductivity (σ_t , σ_e and σ_i) values are shown in Table. 1

The LCO-SDC and LMCO-SDC composite fuel cell conductivity results under different atmospheres at different temperatures are plotted in Fig. 6. The ionic and electronic conductivity of LMCO-SDC was gradually increased compared to LCO-SDC with temperature, indicating the conducting behaviour of the semiconductor composite fuel cell. The lower σ_e and σ_i conductivities of LCO-SDC composite cell may originate from a poor LCO (0.05 S/cm at 600 °C) configuration that provides insufficient reaction sites leading to the triple phase boundary (TPB) for the ORR being only limited to the planar interface between electrode and composite LCO-SDC; meanwhile, the humidified conditions occur at intermediate temperature range resulting in high resistance of the composite cell. When the Mg was a substitute in LCO sites (0.08 S/cm at 600 °C), the grain size was reduced and expected to improve the triple-conducting kinetics involving charges such as protonic, oxygen ionic and electronic ($H^+/O^{2-}/e^-$) at the LMCO-SDC interface. This is borne out and supports the FE-SEM results. From Fig. 6, we observed the LMCO-SDC composite reveals the σ_e and σ_i are almost balanced when compare to LCO-SDC composite cell, resulting in lower electrode polarization and enhancing the fuel cell performance of LMCO-SDC composites.³⁵

Voltage and power density as a function of current density of the Ni-NCAL/SDC/NCAL-Ni (supporting information Figure S3), Ni-NCAL/LCO-SDC/Ni-NCAL and Ni-NCAL/LMCO-SDC/Ni-NCAL composite cells are tested at 500-600 °C by using hydrogen as fuel and ambient air as oxidant, and the results are shown in Fig 7 (a) and (b), respectively. The peak power densities are 0.5, 0.4 and 0.17 W/cm² and open circuit voltages (OCVs) are 0.89, 0.85 and 0.96 V respectively at 600, 550 and 500 °C for the cell with LCO-SDC as a composite material, while the corresponding values are 0.7, 0.54 and 0.4 W/cm² and 1.02, 0.89 and 0.92 V for the cell with LMCO-SDC as a composite material. The enhanced electrochemical performance of LMCO composite is ascribed to Mg²⁺ incorporated into the LiCoO₂ layer, and the Mg²⁺ served as pillars to prevent CoO₂ intraslab from collapse and stabilized the layered structure of LiCoO₂ in its delithiated (Li⁺/H⁺) state at high potentials (Fig.

2). Moreover, it is known that well-developed lithiated layered structures contain the triple charge ($H^+/O^{2-}/e^-$) conducting properties.³ Therefore, we can conclude that the decent electrochemical performance of the assembled cell should be attributed to its sufficient electrical conductivity and high electrocatalytic for fuel oxidation and oxygen reduction. However, it should be noted that our triple conducting LCO-SDC and LMCO-SDC used in our fuel cell devices acted as the electrolyte. According to conventional SOFC science, an electronically conductive material cannot be used for electrolyte, as this will curtail the device's OCV and power output to a serious degree due to the electronic short circuiting problem. However, in stark contrast, our results demonstrated the opposite, as both OCVs and power outputs have shown excellent performance. This is constitutive of the so-called semiconductor-ionic membrane fuel cell technologies. Based on the above studies, the electronic (hole) conduction in mixed p-type semiconductor (LCO or LMCO) and ionic conductor (SDC) may be blocked by a Schottky junction, thus preventing the short circuit problem. In addition, as per our previous reports, the built in field of the Schottky junction can promote the ions (H^+ or O_2) transport, further enhancing the current and power outputs in fuel cell conditions. Thus, such devices can deliver excellent performances.^{17,24,36}

The optical bandgap energy (E_g) of the LCO and LMCO samples were further determined in the wavelength range 300 to 2500 nm by the data of the reflectance versus wavelength plot shown in supporting information Figure S4. The exact energy at which it reflects is estimated using the Kubelka—Munk (K-M) function described as.

$$F(R) = \frac{(1-R)^2}{2R}$$

Where $F(R)$ is the K-M function, R is the reflectance. Fig 8 (a) shows the plot between $[F(R)h\nu]^2$ vs $h\nu$ of the LCO and LMCO samples. As the results presented show, the E_g was reduced from 2.65 to 2.24 eV, when Mg^{2+} ion doped into $LiCoO_2$ sites, resulting in increases to both the Co-O bond length and the concentration of electronic holes. In addition, the narrow band gap of LMCO was clarified by XPS. The XPS valence band maximum (VBM) position for LCO and LMCO are 1.64 and 1.80 eV, respectively, with respect to the Fermi edge at 0 eV binding energy shown in Fig 8 (b). The VBM shifted towards higher BE of the energy axis for LMCO with respect to the LCO, suggesting that for LMCO, the VBM shifted downwards with respect to the LCO. Meanwhile, the conduction band also shift downward with respect to the energy levels of the LCO, and the position of the Fermi level lies close to the valence band, a complete band energy as presented in Fig 8 (c). The narrowing band gap would be favourable to the improvement of the electronic (hole) conductivity of the semiconducting material.³⁷

The durability of LT-SOFCs is also a key impediment for practical applications. We investigated the durability of the Ni-NCAL/LCO-SDC/Ni-NCAL and Ni-NCAL/LMCO-SDC/Ni-NCAL cells operated at a constant current density of 200 mA/cm² at 600 °C, and the voltage recorded as a function of time (h, hours), as shown in Fig 9 (a). The LCO-SDC and LMCO-SDC composite cells are operated under the resulting potential which are 0.18 and 0.79 V respectively, shown in Fig 9 (a). The superior performance of LMCO-SDC composite cell operates with stability for 10 h without significant degradation. In contrast, LCO-SDC composite cell fluctuated after 2 h, with the limitation of LCO-SDC composite mainly due to the redistribution of molecular orbitals between the Co and oxygen during the electro analytical process, and this is explained by using band structure (Energy vs Density of states) shown in Fig. 9 (b-d). The layered rock-salt LiCoO₂ consisting of Co-3d bands are divided by three Co-t_{2g} (valence band) and two Co-e_g (Conduction band) bands.³⁸ Fig. 9 (c) shows the LiCoO₂ band structure before the fuel cell condition. In fuel cell condition, the Li⁺/H⁺ can be extracted from the LiCoO₂, the Co³⁺ ions are oxidized to Co⁴⁺, which is accompanied by a removal of electrons from the Co: t_{2g} band. Meanwhile, the Co: t_{2g} band overlaps on the top of the O²⁻: 2p band shown in Fig. 9 (c). It leads to oxidation of O²⁻ and oxygen loss from the lattice, which is a known reason for the degradation of the fuel cell durability. In contrast, the good durability with higher performance of LMCO-SDC cell could be attributed to the Mg doping on Co sites, as it maintains the Co: t_{2g} band level higher than that of the O²⁻: 2p band and it prevents the oxygen loss from the lattice,^{39,40} shown in Fig 9 (d).

On the other hand, energy band affects not only on electronic conductivity but also on the total electrical properties including ions. By doping excepting LCO energy band gap E_g reduced from 2.65 eV to 2.24 eV, the total conductivities increased from 0.52 S/cm to 1.36 S/cm; in addition, ionic conductivity which is deduced from the fuel cell I-V curves, increased from 0.30 S/cm up to 0.72 S/cm, respectively, at 600 °C. It can be seen from Fig. 6 that the electrical conductivities obtained by EIS increase significantly in correspondence with Mg²⁺ prevent the Co⁴⁺ from overlap into the oxidation state and it does not hinder the Li⁺/H⁺ ion diffusion because it has a similar ionic radii to Li⁺ (0.76 Å) ions. The greater freedom for ionic mobility led to improvement of ionic conduction and mobility as well as commensurate increases in fuel cell device power output. Here, the Ni-NCAL/LMCO-SDC/Ni-NCAL composite cell is shown to be very promising in terms of its results, and its durability has been extended from 2 h (LCO) to 10h (for LMCO). All these improvements are made by band effects on i) the material conductivities both for ionic (from 0.22 S/cm to 0.35 S/cm) and electronic (from 0.142 S/cm to 0.4 S/cm) and ii) the device power output from 0.5 to 0.7 w/cm² with

iii) polarization resistance from $0.85 \Omega \text{ cm}^2$ decreasing to $0.5 \Omega \text{ cm}^2$ and iv) durability enhanced from 2 h to 10 h as compared between the LCO and LMCO devices at 600°C , as shown in Fig 10. Even longer durability demands strong engineering efforts to be continued in ongoing research and development. The results have, at this far demonstrated conclusively and emphatically that semiconductor and band designs have made a new and effective approach to develop next-generation advanced LT-SOFCs.

4. Conclusions

We report on a new approach by design and change energy band structures to make great improvements on the layer structured LCO material properties and their fuel cell performances. The Mg-doped LCO is a hexagonal layered structure with an R3m space group of LCO. The doping made LMCO with a narrower band gap (2.24 eV) than that of LCO (2.65 eV) and produced a significant ionic conductivity enhancement from 0.22 S/cm to 0.35 S/cm. Consequently, the LMCO-SDC device reveals low charge transfer resistance of $0.4 \Omega \text{ cm}^2$ and high power density 0.7 W/cm^2 with good stability at 600°C . The results have demonstrated that designing and changing the band structure can make great impact on material conductivity and the fuel cell device performance, exhibiting great potential and advances for new generation LT-SOFCs.

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Figures:

Fig. 1 XRD patterns of the as-prepared (a) SDC (b) LiCoO_2 (c) $\text{LiMg}_{0.1}\text{Co}_{0.9}\text{O}_2$ and mixed ionic and semiconducting electrodes are (d) LCO-SDC and (e) LMCO-SDC.

Fig. 2 The layered crystal structure of Mg-doped LiCoO_2 .

Fig. 3 FE-SEM micrographs of (a) LiCoO_2 (b) $\text{LiMg}_{0.1}\text{Co}_{0.9}\text{O}_2$ (c) SDC (d) LCO-SDC (e) LMCO-SDC (f) cross sectional image of Ni-NCAL/LMCO-SDC/Ni-NCAL and TEM of (g) LCO-SDC (h) LMCO-SDC composite powders and (i) HR-TEM of LMCO-SDC composite with phases.

Fig. 4 The XPS spectra of LMCO-SDC composite cell core-level emissions. (a) Li (1s), (b) Co (2p), (c) Mg (1s), (d) Ce (3d), (e) Sm (3d) and (f) O (1s).

Fig. 5 Nyquist curves of (a) Ni-NCAL/LCO-SDC/Ni-NCAL and (b) Ni-NCAL/LMCO-SDC/Ni-NCAL fuel cell with equivalent circuit model shown in inset Fig 5 (b).

Fig. 6 Temperature dependence of the ionic and electronic conductivities of LCO-SDC and LMCO-SDC composite cells.

Fig. 7 Typical I-V and I-P curves of (a) Ni-NCAL/LCO-SDC/ Ni-NCAL and (b) Ni-NCAL/LMCO-SDC/ Ni-NCAL fuel cells measured at temperature between 500 °C and 600 °C.

Fig. 8 Durability of (a) LCO-SDC and (b) LMCO-SDC composite cells tested under a constant current density of 200 mA/cm² at 600 °C. And the Energy vs Density of states for (c) LiCoO_2 and the variations of energy bands during the durability test on Fuel cell conditions for (d) LiCoO_2 and (e) $\text{LiMg}_{0.1}\text{Co}_{0.9}\text{O}_2$.

Fig. 9 (a) The optical band gap spectra of the LCO and LMCO samples. And (b) XPS valence band maximum (VBM) of LCO and LMCO, the Fermi energy scale is zero at the VBM and (c) Schematic band energy alignment of LCO and LMCO.

Fig. 10 Schematic diagram of Fuel cell performance, such as Power density, Ionic conductivity and Durability with energy band alignment, Here A: Ni-NCAL/LCO-SDC/Ni-NCAL and B: Ni-NCAL/LMCO-SDC/Ni-NCAL

Fig. 1

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Table. 1 The ionic and electronic conductivity variations with temperature

Temperature (°C)	LCO-SDC (S/cm)		LMCO-SDC (S/cm)	
	σ_i	σ_e	σ_i	σ_e
600	0.22	0.142	0.35	0.4
550	0.143	0.03	0.22	0.242
500	0.06	0.003	0.132	0.126