

**DEVELOPMENT OF COBALTITE AND FERRITE
BASED PEROVSKITE CATHODES FOR
SOLID OXIDE FUEL CELLS**

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**DEPARTMENT OF CHEMICAL ENGINEERING
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by

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Department of Chemical Engineering

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Dedicated To My Beloved Family

Certificate

This is to certify that the thesis entitled “**Development of Cobaltite and Ferrite based Perovskite Cathodes for Solid Oxide Fuel Cells**” being submitted by **Bajnath** to the Department of Chemical Engineering, Indian Institute of Technology Delhi, for the fulfillment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering, is a record of bonafide research work carried out by him. He has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of the thesis.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.



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Baijnath

Abstract

Solid oxide fuel cells (SOFCs) for low/intermediate temperature (500-800 °C) operation have been developed to produce electrical energy and heat. Lanthanum strontium manganite (LSM) and lanthanum strontium cobalt ferrite (LSCF) based perovskites are used as cathodes for yttria-stabilized zirconia (YSZ) and doped ceria electrolyte. LSM-YSZ is used as the composite cathode showing better adherence between cathode and electrolyte layer. The addition of electrolyte in the cathode enhances the oxygen ion conductivity at the cathode electrolyte interface. The LSM electrode reacts with the YSZ electrolyte at high temperature (1200 °C) sintering and forms insulating phases such as lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$, LZ) and strontium zirconate (SrZrO_3 , SZ) at the electrode-electrolyte interface which induce high ohmic and polarization losses. These losses have a large impact on the electrochemical performance of SOFC and have been avoided by using mixed ionic and electronic conductors (MIECs). The MIECs are used as cathode materials for SOFCs and enhances the electrochemical efficiency of SOFCs at low and intermediate temperatures. Single perovskite, strontium-doped lanthanum cobaltite ($\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$; LSCO) cathodes have been synthesized by the different synthesis routes i.e., sol-gel method, glycine-nitrate method, solid-state route, and impregnation method. A comparative study has been done for ionic conductivity and to assess the electrochemical performance of SOFC. It has been found that the electrochemical performance of single perovskite $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cathode is low at higher temperatures hence the brownmillerite-type perovskites Co and/or Mo, as well as Co-Mo co-doping in calcium ferrite cathodes have been carried out to enhance the electrochemical performance of the intermediate temperature SOFC. LSCO cathodes synthesized by different methods have been tested with yttria doped ceria (YDC) and yttria-stabilized zirconia (YSZ) electrolytes in half cells and full cells. Composite anode (NiO-electrolyte) has been used in full cell testing. LSCO synthesized by the sol-gel method provided the highest ionic conductivity of 0.42 S/cm at 700 °C and the lowest activation

energy of 0.32 eV between 500 to 700 °C among all other synthesis methods. LSCO synthesized by the sol-gel method shows the lowest area specific resistance (ASR) of 3.52 Ω cm² at 800 °C for electrolyte supported half-cell (LSCO-YDC/YDC). Electrolyte supported SOFC (LSCO-YSZ/YSZ/NiO-YSZ) with LSCO cathode synthesized by glycine nitrate method provided maximum power density 80.10 mW/cm² (172.83 mA/cm²) at 800 °C (IR-corrected) and ohmic resistance decreases from 5.62 Ω cm² at 700 °C to 2.25 Ω cm² at 800 °C.

LSCO impregnated porous YSZ performed better than other synthesis routes even though low loading of impregnated active material. 5, 7, and 10 wt% LSCO impregnated porous YSZ cathodes have been electrochemically characterized using a 2-probe AC conductivity method. Maximum ionic conductivity of 0.27 S/cm at 800 °C and activation energy of 0.15 eV between 600-800 °C have been observed for 10 wt% LSCO-YSZ cathode. ASR of 1.01 Ω cm² at 800 °C is estimated for the electrolyte supported half cell (10 wt% LSCO-YSZ/YSZ). The electrolyte supported full cell (10 wt% LSCO-YSZ/YSZ/NiO-YSZ) has been tested, and maximum power density 95 mW/cm² (IR-corrected) (189.75 mA/cm²) at 800 °C is observed. The electrolyte supported full cell exhibited 6 Ω cm² electrode polarization at 800 °C in H₂, which is on the higher side leading to low performance.

The performance and stability of cathode materials can be improved by reducing the A-site cation radius, for example, Ca²⁺ substitution at Sr²⁺ or by structure modification to A₂B₂O_{5+ δ} structure. A₂B₂O_{5+ δ} can be crystallized in layered structures (brownmillerite). The brownmillerite structure lattice has perovskite layers of corner-sharing BO₆ octahedra and BO₄ tetrahedra. The oxide ion in the tetrahedral migrates through a unidimensional diffusive passage formed during the ordering of oxygen vacancies along (110) planes. The lattice of these materials can accommodate large oxygen vacancies, which improve the ionic conductivity. These materials provide high MIEC, promising oxygen permeability, and compatible TEC with other cell components. To assess the electrochemical performance of SOFC, brownmillerite-

type structured perovskite such as $\text{Ca}_2\text{Fe}_2\text{O}_5$ (CFO), $\text{Ca}_2\text{Fe}_{1.8}\text{Mo}_{0.2}\text{O}_5$ (CFMO), $\text{Ca}_2\text{Fe}_{1.8}\text{Co}_{0.2}\text{O}_5$ (CFCO), and $\text{Ca}_2\text{Fe}_{1.8}\text{Mo}_{0.1}\text{Co}_{0.1}\text{O}_5$ (CFMCO) cathodes have been synthesized and tested in SOFC. Fe site of parent $\text{Ca}_2\text{Fe}_2\text{O}_5$ structure has been partially substituted by Co and/or Mo, as well as Co-Mo co-doping and tested as cathodes in SOFC. Physical characterization tools such as X-ray diffractometer (XRD), scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscope (TEM), and Brunauer–Emmett–Teller (BET) surface analyzer have been used to assess the phase formation, microstructure, presence of constituent elements, particle size, and surface area of the cathode, respectively. The Co-doped CFO cathodes have better percolation, large surface area, and extended triple phase boundary. Further, the doped CFO cathodes have exhibited chemical compatibility with other cell components during fabrication and cell testing, as evident from SEM micrographs. The effect of porosity in cathode on electrical conductivity has been studied between 600–800 °C. The best electrical conductivity, 0.47 S/cm at 800 °C and the corresponding activation energy of 0.17 eV has been exhibited by CFCO, whereas CFMO and CFMCO cathode shown electrical conductivity 0.11 S/cm and 0.15 S/cm at 800 °C, respectively. Synthesized cathodes have been tested with samarium doped ceria (SDC) and YSZ electrolytes in half cells (such as CFCO-SDC/SDC; CFCO-YSZ/YSZ) and full cells (such as CFCO-SDC/SDC/NiO-SDC; CFCO-YSZ/YSZ/NiO-YSZ). Composite anode (NiO-electrolyte) has been used in full cell testing. CFMO performed better with SDC than YSZ electrolyte between 600–700 °C although the lowest area specific resistance (ASR) of $1.28 \Omega \text{ cm}^2$ at 800 °C has been observed for CFMO with YSZ electrolyte. Similarly, CFMCO provided low ASR at a lower temperature with SDC than that with YSZ electrolyte but exhibited the lowest ASR of $0.41 \Omega \text{ cm}^2$ at 800 °C with YSZ. The CFCO cathode shows lower ASR with YSZ than that with SDC for all the temperatures and provided the lowest value of ASR $0.21 \Omega \text{ cm}^2$ at 800 °C. CFCO cathode has been tested in 900 μm thick electrolyte (SDC/YSZ) supported solid oxide fuel cell (SOFC) CFCO-

SDC/SDC/NiO-SDC and CFCO-YSZ/YSZ/NiO-YSZ provided maximum power densities of 171 and 506 mW/cm² (IR-corrected) at 800 °C, respectively. It is inferred that the CFO based brownmillerite-type structure perovskite cathodes performed better than that of LSCO in the SOFC test condition.

Keywords: SOFC, perovskite cathode, mixed ionic electronic conductor

सार

विद्युत ऊर्जा और ऊष्मा उत्पन्न करने के लिए कम / मध्यवर्ती तापमान (500-800 °C) सॉलिड ऑक्साइड फ्यूल सेल (SOFC) का विकास किया गया है। लैंथेनम स्ट्रॉन्शियम मैंगेनाइट (LSM) एवं लैंथेनम स्ट्रॉन्शियम कोबाल्ट फेराइट (LSCF) आधारित पेरोवस्काइट्स का उपयोग यीट्रिया-स्टेबलाइज्ड जिर्कोनिया (YSZ) और डोण्ड सीरिया इलेक्ट्रोलाइट के लिए कैथोड के रूप में किया जाता है। LSM-YSZ का उपयोग संमिश्रित कैथोड के रूप में किया जाता है जो कैथोड और इलेक्ट्रोलाइट परत के बीच बेहतर पालन करता है। कैथोड में इलेक्ट्रोलाइट का मिश्रण, कैथोड-इलेक्ट्रोलाइट इंटरफेस पर ऑक्सीजन आयन चालकता को बढ़ाता है। LSM इलेक्ट्रोड उच्च तापमान (1200 °C) पर YSZ इलेक्ट्रोलाइट के साथ, इलेक्ट्रोड-इलेक्ट्रोलाइट इंटरफेस पर प्रतिक्रिया करता है और लैंथेनम जिर्कोनेट ($\text{La}_2\text{Zr}_2\text{O}_7$, LZ) और स्ट्रॉन्शियम जिर्कोनेट (SrZrO_3 , SZ) जैसे इन्सुलेटिंग फेजेज का निर्माण करता है, जोकि उच्च ओहमिक और पोलराइजेशन लॉसेस को प्रेरित करते हैं। इन लॉसेस का SOFC की इलेक्ट्रोकेमिकल प्रदर्शन पर नकारात्मक प्रभाव पड़ता है और मिश्रित आयनिक और इलेक्ट्रॉनिक कंडक्टर (MIEC) का उपयोग करके इन लॉसेस से बचा जाता है। MIECs का उपयोग SOFCs के लिए कैथोड मटेरियल्स के रूप में किया जाता है और SOFC की इलेक्ट्रोकेमिकल दक्षता को कम और मध्यवर्ती तापमान पर बढ़ाता है। सिंगल पेरोवस्काइट, स्ट्रॉन्शियम-डोण्ड लैंथेनम कोबाल्टाइट ($\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$; LSCO) कैथोड को विभिन्न संश्लेषण विधियों यानी, सॉल-जेल विधि, ग्लाइसिन-नाइट्रेट विधि, ठोस-अवस्था विधि और इम्प्रेगनेशन विधि द्वारा संश्लेषित किया गया है। आयनिक चालकता के लिए और SOFC की इलेक्ट्रोकेमिकल प्रदर्शन का आकलन करने के लिए एक तुलनात्मक अध्ययन किया गया है। यह पाया गया है कि सिंगल पेरोवस्काइट $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ कैथोड का इलेक्ट्रोकेमिकल प्रदर्शन उच्च तापमान पर कम होता है, इसलिए मध्यवर्ती तापमान SOFC की इलेक्ट्रोकेमिकल प्रदर्शन को बढ़ाने के लिए, ब्राउनमिलीराइट-प्रकार के पेरोवस्काइट्स कैल्शियम फेराइट कैथोड में, Co या Mo, और Co-Mo को-डोपिंग किया गया है। विभिन्न विधियों से संश्लेषित LSCO कैथोड को हॉफ सेल और फुल सेल में यीट्रिया-डोण्ड सीरिया (YDC) और यीट्रिया-स्टेबलाइज्ड जिर्कोनिया (YSZ) इलेक्ट्रोलाइट्स के साथ परीक्षण किया गया है। फुल सेल परीक्षण में संमिश्रित एनोड (NiO-इलेक्ट्रोलाइट) का उपयोग किया गया है। अन्य सभी संश्लेषण विधियों के बीच, सॉल-जेल विधि द्वारा संश्लेषित LSCO ने 700 °C पर 0.42 S/cm की उच्चतम आयनिक चालकता और 500 से 700 °C के बीच 0.32 eV की सबसे कम सक्रियण ऊर्जा प्रदान की। सॉल-जेल विधि द्वारा संश्लेषित LSCO, इलेक्ट्रोलाइट सपोर्टेड हॉफ सेल (LSCO-YDC/YDC) के लिए, 800 °C पर $3.52 \Omega \text{ cm}^2$ का सबसे कम एरिया स्पेसिफिक रजिस्टेंस (ASR) दिखाता है। इलेक्ट्रोलाइट सपोर्टेड SOFC (LSCO-YSZ/YSZ/NiO-YSZ), ग्लाइसिन नाइट्रेट विधि द्वारा संश्लेषित LSCO कैथोड के साथ, अधिकतम पॉवर डेंसिटी 800 °C पर 80.10 mW/cm^2 (172.82

mA/cm²) (IR-संशोधित), और ओहमिक रजिस्टेंस 700 °C पर 5.62 Ω cm² से कम होकर 800 °C पर 2.25 Ω cm² हो जाता है।

LSCO इम्प्रेग्नेटेड पोरस YSZ, अन्य संश्लेषण विधियों से बेहतर प्रदर्शन किया, भले ही इम्प्रेग्नेटेड एक्टिव मटेरियल की लोडिंग कम हो। 5, 7, और 10 wt% LSCO इम्प्रेग्नेटेड पोरस YSZ कैथोड को 2-प्रोब एसी चालकता विधि का उपयोग करके इलेक्ट्रोकेमिकल प्रदर्शन की जांच की गई है। 800 °C पर 0.27 S/cm की अधिकतम आयनिक चालकता और 600-800 °C के बीच 0.15 eV की सक्रियण ऊर्जा, 10 wt% LSCO-YSZ कैथोड के लिए देखी गई है। 800 °C पर 1.01 Ω cm² का ASR इलेक्ट्रोलाइट सपोर्टेड हॉफ सेल (10 wt% LSCO-YSZ/YSZ) के लिए अनुमानित है। इलेक्ट्रोलाइट सपोर्टेड फुल सेल (10 wt% LSCO-YSZ/YSZ/NiO-YSZ) का परीक्षण किया गया है, और 800 °C पर अधिकतम पॉवर डेंसिटी 95 mW/cm² (189.75 mA/cm²) (IR-संशोधित) प्राप्त हुई। इलेक्ट्रोलाइट सपोर्टेड फुल सेल ने H₂ में 800 °C पर 6 Ω cm² इलेक्ट्रोड पोलराइजेशन का प्रदर्शन किया, जो कि उच्च है और कम इलेक्ट्रोकेमिकल प्रदर्शन का कारण है।

कैथोड मटेरियल्स के प्रदर्शन और स्टेबिलिटी को A-साइट कैटायन त्रिज्या को कम करके बेहतर बनाया जा सकता है, उदाहरण के लिए, Sr²⁺ पर Ca²⁺ प्रतिस्थापन या A₂B₂O_{5+δ} संरचना में संरचना संशोधन द्वारा। A₂B₂O_{5+δ} को लेयर्ड स्ट्रक्चर (ब्राउनमिलीराइट) में क्रिस्टलाइज्ड किया जा सकता है। ब्राउनमिलीराइट स्ट्रक्चर लैटिस में कोने-साझाकरण BO₆ ऑक्टाहेड्रा और BO₄ टेट्राहेड्रा की पेरोवस्काइट परतें हैं। टेट्राहेड्रल में ऑक्साइड आयन, ऑक्सीजन रिक्तियों (110) के साथ ऑक्सीजन रिक्तियों के आदेश के दौरान गठित एक यूनीडायमेंशनल डिफ्यूजिव पैसेज से गुजरता है। इन मटेरियल्स के लैटिस बड़ी ऑक्सीजन रिक्तियों को समायोजित कर सकती है, जो आयनिक चालकता में सुधार करती है। ये मटेरियल्स उच्च MIEC, प्रॉमिसिंग ऑक्सीजन पारगम्यता, और अन्य सेल घटकों के साथ संगत TEC प्रदान करते हैं। SOFC के इलेक्ट्रोकेमिकल प्रदर्शन का आकलन करने के लिए, ब्राउनमिलीराइट-प्रकार के स्ट्रक्चर्ड पेरोवस्काइट जैसे Ca₂Fe₂O₅ (CFO), Ca₂Fe_{1.8}Mo_{0.2}O₅ (CFMO), Ca₂Fe_{1.8}Co_{0.2}O₅ (CFCO), और Ca₂Fe_{1.8}Mo_{0.1}Co_{0.1}O₅ (CFMCO) को संश्लेषित किया गया है और SOFC में प्रदर्शन के लिए परीक्षण किया गया है। पेरेंट Ca₂Fe₂O₅ संरचना की Fe साइट को आंशिक रूप से Co और / या Mo, और Co-Mo को-डोपिंग द्वारा प्रतिस्थापित किया गया है, और SOFC में कैथोड के रूप में परीक्षण किया गया है। भौतिक लक्षण वर्णन उपकरण जैसे एक्स-रे डिफ्रेक्टोमीटर (XRD), स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोप (SEM), एनर्जी-डिस्पर्सिव एक्स-रे स्पेक्ट्रोस्कोपी (EDX), ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोप (TEM), और ब्रूनर-एम्मेट-टेलर (BET) सरफेस एनालाइजर को क्रमशः फेज फार्मेशन, माइक्रोस्ट्रक्चर, घटक तत्वों की उपस्थिति, कण आकार, और कैथोड की सतह क्षेत्र का आकलन करने के लिए उपयोग किया गया है। सह-डोप किए गए CFO कैथोड में बेहतर परकोलेशन, बड़े सतह क्षेत्र और विस्तारित ट्रिपल फेज सीमा होती है। इसके अलावा, डोप्ड CFO कैथोड ने SEM

माइक्रोग्राफ से स्पष्ट रूप में निर्माण और सेल परीक्षण के दौरान अन्य सेल घटकों के साथ रासायनिक संगतता प्रदर्शित की है। विद्युत चालकता पर कैथोड में पोरोसिटी का प्रभाव 600-800 °C के बीच अध्ययन किया गया है। सर्वोत्तम विद्युत चालकता, 800 °C पर 0.47 S/cm और 0.17 eV की सक्रियण ऊर्जा को CFÇO द्वारा प्रदर्शित किया गया है, जबकि CFMO और CFMCO कैथोड में विद्युत चालकता 800 °C पर 0.11 S/cm और 0.15 S/cm क्रमशः दिखाया गया है। संश्लेषित कैथोड को समेरियम-डोपड सीरिया (SDC) और YSZ इलेक्ट्रोलाइट्स के साथ हॉफ सेल (जैसे कि CFÇO-SDC/SDC; CFÇO-YSZ/YSZ) और फुल सेल (जैसे कि CFÇO-SDC/SDC/NiO-SDC; CFÇO-YSZ/YSZ/NiO-YSZ) में परीक्षण किया गया है। फुल सेल परीक्षण में संमिश्रित एनोड (NiO-इलेक्ट्रोलाइट) का उपयोग किया गया है। CFMO ने 600-700 °C के बीच YSZ इलेक्ट्रोलाइट की तुलना में SDC के साथ बेहतर प्रदर्शन किया, हालांकि 800 °C पर $1.28 \Omega \text{ cm}^2$ का सबसे कम एरिया स्पेसिफिक रजिस्टेंस (ASR) YSZ इलेक्ट्रोलाइट के साथ CFMO के लिए देखा गया है। इसी तरह, CFMCO ने YSZ की तुलना में SDC इलेक्ट्रोलाइट के साथ कम तापमान पर कम ASR प्रदान किया लेकिन YSZ के साथ 800 °C पर $0.41 \Omega \text{ cm}^2$ के सबसे कम ASR का प्रदर्शन किया। CFÇO कैथोड सभी तापमानों के लिए SDC की तुलना में YSZ के साथ ASR को कम दिखाता है और 800 °C पर ASR $0.21 \Omega \text{ cm}^2$ का न्यूनतम वैल्यू प्रदान करता है। CFÇO कैथोड का परीक्षण 900 माइक्रोन मोटी इलेक्ट्रोलाइट (SDC/YSZ) सपोर्टेड सॉलिड ऑक्साइड फ्यूल सेल (SOFC) में किया गया है, CFÇO-SDC/SDC/NiO-SDC और CFÇO-YSZ/YSZ/NiO-YSZ ने 800 °C पर क्रमशः 171 और 506 mW/cm^2 (IR-संशोधित) की अधिकतम पॉवर डेन्सिटीज प्रदान की। SOFC परीक्षण की स्थिति में, यह अनुमान लगाया गया है कि CFO आधारित ब्राउनमिलीराइट-प्रकार के स्ट्रक्चर्ड पेरोवस्काइट कैथोड LSCO की तुलना में बेहतर प्रदर्शन करते हैं।

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