MECHANISTIC APPROACHES IN THE DESIGN OF CATHODE AND ANODE MATERIALS FOR SOLID OXIDE FUEL CELLS

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JULY 2019

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by

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Submitted
in fulfilment of the requirements of the degree of Doctor of Philosophy
to the

Indian Institute of Technology Delhi
July 2019

Dedicated to my Parents and All the Women…….

Certificate

This is to certify that the dissertation entitled "**Mechanistic Approaches in the Design of Cathode and Anode Materials for Solid Oxide Fuel Cells**" being submitted by **Uzma Anjum** to the Indian Institute of Technology Delhi, for fulfillment of the requirements for the award of **Doctor of Philosophy** in Chemical Engineering is a record of bona-fide research work carried out by her. She 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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Acknowledgements

All praises are due to Allah for blessing me with the energy, time and motivation to work on this project. I bow to the Almighty, the merciful, the compassionate, for showering His choicest blessings on me to go through the ups and downs of life and enabling me to put in my best to complete this endeavor and for bestowing me with affectionate and caring parents.

Undertaking this Ph.D. has been a truly life-changing experience for me and it would not have been possible to do it without the support and guidance that I received from many people.

First and foremost, I want to thank my supervisor Professor M. Ali Haider. It has been an honour to be his Ph.D. student. He has taught me, both consciously and subconsciously, how good research is done. I appreciate all his contributions of time, ideas, and to make my Ph.D. experience productive and stimulating. The joy and enthusiasm he has for his research was motivational for me, even during tough times in the Ph.D. pursuit. He always inspired me by his hardworking and passionate attitude. He has always made himself available to clarify my doubts despite his busy schedules and I consider it as a great opportunity to do my doctoral programme under his guidance and to learn from his research expertise.

Besides my supervisor, I would like to thank my review committee members (Prof. S.Basu Prof. Anupam Shukla and Prof. Josemon Jacob) for their great support and invaluable advice, scholarly inputs and consistent encouragement throughout the research work.

My sincere thanks to Dr. Md. Imteyaz Alam, and Dr. Tuhin Suvra Khan, Post-Doctoral Fellows in the REC lab who were always there to help me with the problems related to my work. Dr. Tuhin Suvra Khan helped me in understanding the fundamentals of the theoretical work. Their friendly nature made the learning process a lot easier. Dr. Md. Imteyaz Alam, Ms Shelaka Gupta, and Ms. Fatima Jalid have always been the motivational support who inspired me throughout my Ph.D. journey. I would like to express my sincere thanks to Dr. Manish Agarwal

and his HPC team at Computer Service Center, for providing help in resolving the software installation and its execution issues on high performance computing cluster at IIT Delhi. Apart from help in HPC, Dr. Manish Agarwal has helped me in setting up calculations on LAMMPS, His scientific input and rigorous discussions have helped me producing many research articles in my Ph.D. I am also thankful to Dr. Nishant K. Sinha, Research Engineer, The Boeing Company, for his initial help in the theoretical calculations. I am really thankful to Dr. Pankaj Tiwari, Post-Doctoral Fellows at the Fuel Cell Lab at IIT Delhi, for his initial help in setting up and running the experiments.

I gratefully acknowledge IIT Delhi for the financial support through IIT fellowship that made my Ph.D. work possible. I would also like to thank the administrative and technical staff members of IIT Delhi who have been kind enough to advise and help in their respective roles.

My generous thanks to my lab mates, Ms. Fatima Jalid, , Mr. Saleem Akhtar Farooqui, Mr. Saurabh Mishra, Mr. Sonit Balyan, Ms. Haseena K V, Dr. Neetu Kumari, Dr. Madhulika Gupta, Dr. Gourav Shrivastav, Mr. Sarwar Hussain, Ms. Trishya whom I have shared this journey. I would also like to extend my heartfelt gratitude and to my hostel mates Ms. Shabina Ashraf, Ms. Shelaka Gupta, Ms. Ieeba Khan, and Ms. Nusrat who have shown their support in a very special way, and I gained a lot from them, through their personal and scholarly interactions, their suggestions at various points of my research program. I would like to especial thank to my dear friends Aisha, Sufia, Suhiab, Fatimah, Shelaka, Afkham and Uzma ; without their love, care and advice, this journey would have not been that easier and pleasant.

Patience is prerequisite for an investigation and support of my family has made me strong enough to hold on the time and make every moment fruitful. I thank my parents, Mrs. Nargis Parveen and Mr. Abdul Sattar, who encouraged and helped me at every stage of my personal and academic life, and longed to see this achievement come true. They are my ultimate role models. I would also like to express my deepest gratitude to my husband Dr. Suhaib Fazal for

providing me with unfailing support and continuous encouragement through the process of researching and writing this thesis. My deep appreciation goes to my siblings, Farah Baji, Sumera, Ifra, Tanazza, Asma, Aqsa and Abdul Basit who have always been there to motivate me and fortified me during the tough times. They have been there in more ways than they can realize.

Uzma Anjum

Abstract

Development of an intermediate temperature (operating at 973 K or less) solid oxide fuel cell (SOFC) necessitates the design of efficient electrode materials to carry out oxygen reduction reaction (ORR) and transport at the cathode and oxidation of hydrocarbon fuels at the anode. Towards this, ORR in double perovskites materials of series $LnBa_{1-x}Sr_xCo_yFe_{1-y}O_{5+\delta}$ (LnBSCF, Ln = Gd, Pr) was studied. Molecular dynamics (MD) simulations were utilized to calculate the oxygen anion diffusivity (D) in the lattice of the double perovskite structured materials. In general, anisotropicity in oxygen transport was observed. For example, oxygen anion diffusion coefficient for the $PrBaCo_2O_{5+\delta}$ (PBCO) material was calculated to be $3 \text{ x } 10^{-8}$ cm^2 s^{-1} at 873 K in the *a-b* (Pr-O and Co-O) direction, which was observed to be higher than in the Ba-O plane ($D = 8\text{x}10^{-9}$ cm^2 s^{-1} at 873 K). On doping, PBCO with Sr and Fe cations, the resultant $PrBa_{1-x}Sr_xCo_yFe_{1-y}O_{5+\delta}$ (PBSCF) structure was calculated to show an order of magnitude higher diffusivity ($D = 1.1\text{x}10^{--7}$ cm^2 s^{-1} at 873 K) as compared to PBCO. Trends in calculated diffusion coefficients compared well with the measured electrocatalytic activity of the material reported in other experimental studies. The electrochemical measurements were performed on a geometrically well-defined nanostructured thin-film electrode, fabricated as a symmetric cell using a spray pyrolysis deposition method. Electrochemical experiments on thin-film electrodes provided an insight into the operating mechanism. Following the hypothesis of a characteristic thickness (L_c) below which the performance was expected to be predominantly controlled by surface reaction, the L_c for layered perovskite PBSCF at 863 K was calculated to be around 3.2 μm. Interestingly, the dense thin-film electrode of PBSCF (1 to 3 μm thick) deposited using the spray pyrolysis method showed a thickness dependent electrochemical performance suggesting bulk diffusion limitation.

In order to understand the origin of this diffusion limited electrochemical performance, density functional theory (DFT) calculations were utilized to calculate the surface energy (γ) and oxygen vacancy (E_{OV}) formation energies in the respective layered structures of PBCO, PBSCF and GBCO. For example, the E_{OV} in the Gd plane (98.4 kJ/mol) of $GdBaCo_2O_{5+\delta}$ (GBCO) was calculated to be lower than that of Ba plane (E_{OV} = 266.3 kJ/mol). However, the surface energy of the Ba plane was calculated to be minimum (γ =7.2 kJ/mol Å), which makes it the most exposed surface, while it is least diffusive. Due to low surface energy values, Ba cations are known to segregate towards the surface of the double perovskite structure. GBCO nanoparticles of reduced size were expected to provide a desired control on the degree of segregation of the Ba cation. The particle size of GBCO was reduced to 20 nm using a bio-milling approach,

wherein the chemically synthesized particles were subjected to fermentation using a microorganism. The measured impedance of the electrode made up of bio-milled nanoparticles was improved by 15% as compared to the chemically synthesized material. MD simulation on the GBCO nanoparticles indicated two distinct regimes of diffusion; one corresponding to the surface and other to the bulk region of the nanoparticle. The thickness (2 nm) of surface shell regime was observed to be particle size independent. The diffusivity of the shell regime (D = 3.9×10^{-10} cm^2 s^{-1} at 873 K) was calculated similar to that of the core (D = 2.51×10^{-10} cm^2 s^{-1} at 873 K). Thus, nanoparticles showed improved electrochemical performance as compared to the bulk electrode, likely due to reduced Ba cation segregation in nanostructured electrode. In a similar mechanistic approach, for the design of anode materials, an *ab-initio* microkinetic model (MKM) was constructed to screen electrocatalytic activity of the transition metal catalysts (Ag, Au, Cu, Pd, Pt, Co, Ni, Ru, Ru, and Re) for H_2 and CO oxidation at low, intermediate and high operating temperatures of a SOFC. The MKM utilized two descriptors; carbon and oxygen binding energies on the surface of the metal catalysts, to describe the trend in turn over frequency for the desired reaction at the open circuit voltage and on applying a potential bias. The MKM was further implemented to design a bimetallic alloy catalyst to achieve maximum theoretical activity as described by the Sabatier principle. Pt_3Ni, Pt_3Co, and Cu_3Rh were observed to be the best anode catalysts for intermediate temperature (873 K) operations.

सार

एक मध्यवर्ती तापमान का विकास (973 K या उससे कम) ठोस ऑक्साइड ईंधन सेल (SOFC) का संचालन ऑक्सीजन की कमी प्रतिक्रिया (ORR) को पूरा करने के लिए कुशल इलेक्ट्रोड सामग्री के डिजाइन की आवश्यकता होती है और एनोड पर हाइड्रोबेनिक ईंधन के कैथोड और ऑक्सीकरण पर परिवहन होता है। इसकी ओर, श्रृंखला $LnBa_{1-x}Sr_xCo_yFe_{1-y}O_{5+\delta}$ (LnBSCF, Ln = Gd, Pr) के दोहरे पर्कोसाइट्स सामग्रियों में (ORR) का अध्ययन किया गया। आणविक गतिशीलता (MD) सिमुलेशन का उपयोग डबल पेरोसाइट संरचित सामग्री के जाली में ऑक्सीजन आयनों डिफिसिटिविटी (डी) की गणना करने के लिए किया गया था। सामान्य तौर पर, ऑक्सीजन परिवहन में एनिसोट्रोपिसिटी देखी गई थी। उदाहरण के लिए, $PrBaCo_2O_{5+\delta}$ (PBCO) सामग्री के लिए ऑक्सीजन आयनों के प्रसार गुणांक की गणना 3 x 10^{-8} cm^2 s^{-1} में 873 K पर *a-b* (Pr-O और Co-O) दिशा में की गई थी, जिसे देखा गया था Ba-O सतह (D = 8 x 10^{-9} cm^2 s^{-1} 873 K पर) से अधिक हो। डोपिंग पर, पीबीसीओ सीनियर और एफए के साथ, परिणामी $PrBa_{1-x}Sr_xCo_yFe_{1-y}O_{5+\delta}$ (PBSCF) संरचना को परिमाण के अंतर को उच्च दिखाने के लिए गणना की गई थी (D = 1.1 x 10^{-7} cm^2 s^{-1} 873 K पर) पीबीसीओ की तुलना में। अन्य प्रायोगिक अध्ययनों में रिपोर्ट की गई सामग्री की मापित इलेक्ट्रोकैटलिटिक गतिविधि के साथ तुलनात्मक रूप से गणना प्रसार गुणांक में रुझान। विद्युत रासायनिक माप एक ज्यामितीय रूप से अच्छी तरह से परिभाषित नैनोट्रक्टेड पतली-फिल्म इलेक्ट्रोड पर किए गए थे, एक स्प्रे पाइरोलिसिस बयान विधि का उपयोग करके एक सममित सेल के रूप में गढ़ा गया। पतली फिल्म इलेक्ट्रोड पर विद्युत रासायनिक प्रयोगों ने ऑपरेटिंग तंत्र में एक अंतर्दृष्टि प्रदान की। नीचे एक विशेषता मोटाई (L_c) की परिकल्पना के बाद, जिसके प्रदर्शन की उम्मीद मुख्य रूप से सतह की प्रतिक्रिया से नियंत्रित की जाती थी, 863 K पर स्तरित पर्कोवसाइट PBSCF के लिए L_c की गणना लगभग 3.2 µm की गई थी। दिलचस्प है, पीबीएससीएफ (1 से 3 µm) के घने पतले फिल्म इलेक्ट्रोड को स्प्रे पाइरोलिसिस विधि का उपयोग करके जमा किया गया था, जिसमें एक मोटाई पर निर्भर विद्युत रासायनिक प्रदर्शन दिखाया गया था जो थोक प्रसार सीमा का सुझाव देता है।

इस प्रसार सीमित विद्युत रासायनिक प्रदर्शन की उत्पत्ति को समझने के लिए, पीबीसीओ, पीबीएससीएफ और जीबीसीओ की संबंधित स्तरित संरचनाओं में सतह ऊर्जा (γ) और ऑक्सीजन रिक्ति (E_{OV}) गठन ऊर्जा की गणना करने के लिए घनत्व कार्यात्मक सिद्धांत (डीएफटी) गणना का उपयोग किया गया था। उदाहरण के लिए, $GdBaCo_2O_{5+\delta}$ (GBCO) के Gd प्लेन (E_{OV} = 98.4 kJ / mol) में E_{OV} की गणना Ba प्लेन (E_{OV} = 266.3 kJ/mol) की तुलना में कम की गई थी। हालांकि, Ba सतह की सतह ऊर्जा न्यूनतम (Υ = 7.2 kJ/mol $Å^2$) होने की गणना की गई थी, जो इसे सबसे अधिक उजागर सतह बनाती है, जबकि यह कम से कम विसरित है। कम सतह ऊर्जा मूल्यों के कारण, Ba

फैटायनों को डबल पर्कोसाइट्स संरचना की सतह की ओर अलग करने के लिए जाना जाता है। कम आकार के GBCO नैनोकणों से उम्मीद की जा रही थी कि वे Ba उद्धरण के पृथक्करण की डिग्री पर एक वांछित नियंत्रण प्रदान करें। जैव-मिलिंग दृष्टिकोण का उपयोग करके GBCO के कण आकार को 20 nm तक कम कर दिया गया था, जिसमें सूक्ष्मजीवों का उपयोग करके रासायनिक रूप से संश्लेषित कणों को किण्वन के अधीन किया गया था। बायो-मिल्ड नैनोपार्टिकल्स से बने इलेक्ट्रोड के मापा प्रतिबाधा को रासायनिक रूप से संश्लेषित सामग्री की तुलना में 15% सुधार हुआ था। GBCO नैनोकणों पर एमडी सिमुलेशन ने प्रसार के दो अलग-अलग शासनों का संकेत दिया; एक सतह और अन्य नैनोकणों के थोक क्षेत्र के लिए इसी। सतह खोल शासन की मोटाई (2 nm) कण आकार स्वतंत्र होने के लिए मनाया गया था। शेल शासन की विविधता (873 K पर $D = 3.9 \times 10^{-10}$ cm^2 s^{-1}) की गणना कोर ($D = 2.51 \times 10^{-10}$ cm^2 s^{-1} 873 K) के समान की गई थी। इस प्रकार, नैनोकणों ने इलेक्ट्रोकेमिकल प्रदर्शन को थोक इलेक्ट्रोड की तुलना में बेहतर दिखाया है, संभवत: नैनोस्ट्रक्चर किए गए इलेक्ट्रोड में Ba कटाव अलगाव के कारण। एक समान यंत्रवत दृष्टिकोण में, एनोड सामग्रियों के डिजाइन के लिए, एब-इनिटियो माइक्रोकैनेटिक मॉडल (एमकेएम) का निर्माण संक्रमण धातु उत्प्रेरकों की इलेक्ट्रोकैटलिटिक गतिविधि (Ag, Au, Cu, Pd, Pt, Co, Ni, Ru, आर, Re) के लिए किया गया था। एक SOFC के कम, मध्यवर्ती और उच्च ऑपरेटिंग तापमान पर H_2 और CO ऑक्सीकरण के लिए Ru, और Re)। एमकेएम ने दो डिस्क्रिप्टर का उपयोग किया; धातु उत्प्रेरक की सतह पर कार्बन और ऑक्सीजन बाध्यकारी ऊर्जा, खुले सर्किट वोल्टेज पर वांछित प्रतिक्रिया के लिए आवृत्ति पर आवृत्ति का वर्णन करने के लिए और एक संभावित पूर्वाग्रह को लागू करने के लिए। एमकेएम को साबाटियर सिद्धांत द्वारा वर्णित अधिकतम सैद्धांतिक गतिविधि को प्राप्त करने के लिए एक द्विधात्विक मिश्र धातु उत्प्रेरक डिजाइन करने के लिए लागू किया गया था। Pt_3Ni, Pt_3Co, और Cu_3Rh को मध्यवर्ती तापमान (873 K) के संचालन के लिए सर्वश्रेष्ठ एनोड उत्प्रेरक माना गया।

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