

DEVELOPMENT OF CERIA BASED CATALYST FOR SOLID OXIDE CELL FOR CARBON DIOXIDE REDUCTION

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by

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Dedicated to my husband (Chandan Sharma) and parents

Certificate

This is to certify that the thesis entitled “**Development of Ceria Based Catalyst for Solid Oxide Cell for Carbon Dioxide Reduction**” being submitted by **Neetu Kumari** to the Indian Institute of Technology Delhi for fulfillment of the requirements for the ward of **Doctor of Philosophy** in Chemical Engineering is a record of bona fide research work carried out by her. She has worked under our supervision and has fulfilled the requirements, which to our 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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Abstract

Density functional theory (DFT) calculations are performed to study the mechanism of carbon dioxide (CO_2) reduction to carbon monoxide (CO) and methanol (CH_3OH) on $\text{CeO}_2(110)$ surface. Thermochemistry of elementary steps for the suggested routes of CO_2 reduction to CH_3OH is evaluated on stoichiometric ceria surface. Calculations are performed to determine the most favorable adsorption orientation and corresponding binding energy of reaction intermediates. Mechanistic routes via the formation of the carboxyl (COOH) or the formate (HCOO) intermediate species are considered. Formate is observed to be more stable, with a binding energy of $-222.9 \text{ kJ mol}^{-1}$, on the surface of the stoichiometric ceria as compared to the carboxyl ($\Delta E_{\text{binding}} = -36.0 \text{ kJ mol}^{-1}$). Formate species on subsequent hydrogenation produce H_2COOH . In order to produce methanol, H_2COOH is required to dissociate into H_2CO and OH which is a significantly endothermic ($\Delta E_{\text{rxn}} = 64.0 \text{ kJ mol}^{-1}$) step. On the contrary, the overall route involving a carboxyl intermediate is exothermic, on stoichiometric, except for the dissociation of COOH into CO and OH ($\text{COOH} \rightarrow \text{CO} + \text{OH}$) which is endothermic by 5.0 kJ mol^{-1} . On reduced ceria surface, CO_2 dissociates to CO on interacting with the oxygen vacancy. The oxygen atom heals the vacancy site and regenerates the stoichiometric surface via a redox mechanism with intrinsic activation and reaction energies of $259.2 \text{ kJ mol}^{-1}$ and 238 kJ mol^{-1} respectively. Lateral interaction of oxygen vacancies are studied by the generation of two oxygen vacancies per unit of CeO_2 surface. Compared to a single isolated vacancy, the activation and reaction energies of CO_2 dissociation on a di-vacancy are approximately reduced to half of its value. Hydrogen atom co-adsorbed on the reduced surface is observed to assist CO_2 dissociation by forming a carboxyl intermediate, $\text{CO}_2 + \text{H} \rightarrow \text{COOH}$ ($\Delta E_{\text{act}} = 39.0 \text{ kJ mol}^{-1}$, $\Delta H = -69.2 \text{ kJ mol}^{-1}$) which on subsequent dissociation produces CO via the redox mechanism. On hydrogenation, CO is likely to produce methanol on reduced ceria surface. The energetics of CO hydrogenation to produce methanol showed exothermic steps with activation barriers comparable to the DFT calculations reported for $\text{Cu}(111)$ and $\text{CeO}_{2-x}/\text{Cu}(111)$ interface, indicating an extended ceria surface is equally active to reduce CO_2 into CO and CH_3OH . Further doping of ceria surface with aliovalent metal cation (Gd , Sm and Pr) could facilitate the facile oxygen vacancy formation and improve the electronic and ionic conductivity inside the ceria lattice, leading to enhance the electrocatalytic activity for CO_2 reduction reaction.

Molecular dynamic simulations are performed to determine the oxygen anion diffusivity in pure ceria (CeO_2) and doped ceria $\text{M}_x\text{Ce}_{1-x}\text{O}_{2-0.5x}$ ($\text{M}=\text{Gd}$, Sm and Pr) with varying level of dopant concentration from 5-30% ($x = 0.05-0.3$). Doping with Gd showed an improvement in oxygen anion diffusivity value by two order of magnitude ($D = 4.67 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 1173 K) as compared to the undoped ceria ($D = 1.33 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at 1173 K). 10% of doping level was estimated as the optimum concentration of all the dopants at which all of the doped ceria materials showed maximum diffusivity of oxygen anion. Among the three dopants studied, Pr was observed to show maximum diffusivity of oxygen anion in the temperature range of 773-1173 K of simulations.

By utilizing $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC) and $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (PDC) composited with copper as cathode materials, solid oxide cells are fabricated. Infiltration technique is employed to impregnate: Cu-GDC and Cu-PDC electrodes into the yttria stabilized zirconia (YSZ) scaffold. Dense YSZ phase is used as electrolyte and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) is used as anode of SOEC. The polarization resistance of the cell with Cu-PDC cathode are measured to be of relatively lower value $17.9 \text{ } \Omega \text{ cm}^2$ and $5.1 \text{ } \Omega \text{ cm}^2$ as compared to the corresponding $23.8 \text{ } \Omega \text{ cm}^2$ and $7.5 \text{ } \Omega \text{ cm}^2$ on Cu-GDC electrode for CO_2/H_2 ratio of 92/08 and 28/82 respectively. Similarly, CO_2 electrolysis current on Cu-PDC cathode are measured relatively higher to the values of -0.056 A cm^{-2} at $\text{CO}_2/\text{H}_2 = 76/24$, -0.069 A cm^{-2} at $\text{CO}_2/\text{H}_2 = 56/44$ and -0.075 A cm^{-2} at $\text{CO}_2/\text{H}_2 = 38/62$. Impedance spectra of Cu-PDC cathode are measured at varying potential, indicated a significant decrease in polarization resistance from $17.9 \text{ } \Omega \text{ cm}^2$ to $6.3 \text{ } \Omega \text{ cm}^2$ as the applied potential increased from OCV (-0.89 V) to -1.6 V at $\text{CO}_2/\text{H}_2=92/08$. Results suggested an improved electrocatalytic activity of Cu-PDC cathode as compared to Cu-GDC electrode. However the electrochemical performance of cell with Cu-PDC cathode, fabricated by infiltration method, is limited to a low reduction current (-0.075 A cm^{-2} at 2.0 V).

In order to modify the morphology of the cathode electrocatalyst, the fabrication technique is altered and solid oxide cell prepared by using solid state method with Cu-PDC cathode, LSM anode and YSZ as electrolyte. By varying the applied potentials and reducing environment at different volumetric ratio of CO_2/CO and CO_2/H_2 electrochemical measurements are carried out to understand the role of reducing atmosphere. Polarization resistance of the Cu- $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ electrode is observed to decrease from $44.0 \text{ } \Omega \text{ cm}^2$ ($\text{CO}_2/\text{CO}=93/07$) to $7.0 \text{ } \Omega \text{ cm}^2$ ($\text{CO}_2/\text{CO}=23/77$) with the increase of CO and similarly from $7.5 \text{ } \Omega \text{ cm}^2$ ($\text{CO}_2/\text{H}_2=97/03$) to $1.0 \text{ } \Omega \text{ cm}^2$ ($\text{CO}_2/\text{H}_2=24/76$) with the increase in H_2 concentration. On varying proportions of CO_2/H_2 and

CO₂/CO, a maximum reduction current of -0.84 A cm⁻² (V_{app}=2.5V) and -0.12 A cm⁻² (V_{app}=1.5V) is measured for 75/25 CO₂/H₂ and 93/07 CO₂/CO respectively. The solid state fabricated Cu-PDC cathode has shown an improved electrochemical performance with higher reduction current of -0.50 A cm⁻² at 2.0 V as compared to the infiltrated Cu-PDC cathode (-0.049 A cm⁻² at 2.0 V) at the similar ratio of CO₂/H₂ (~75/25) at temperature 1023 K. CO₂ conversion is achieved up to 11% with a faradic efficiency for CO production of 99% at the applied potential of 2.5 V (CO₂/H₂ ratio of 75/25).

Spray pyrolysis strategy is applied to prepare a dense phase microstructure of PDC based cathode layer on the dense YSZ substrate. Over the dense PDC thin film (thickness ~ 400 nm), Cu nitrate precursor is injected and calcined at 673 K. The total polarization resistance of cell, with spray coated Cu-PDC cathode, is relatively lower (7.10 Ω cm²) as compared to the Cu-PDC fabricated by solid state (7.90 Ω cm²) and infiltration techniques (17.9 Ω cm²) for the similar ratio of CO₂/H₂ (~ 92/08) at 1023 K, suggesting spray coated PDC, having dense phase microstructure, could offer a minimal charge transfer resistance as compared to infiltrated and solid state prepared cathode component. However, the maximum reduction current measured at 2.5 V potential, is lower in case of spray deposited Cu-PDC cathode (-0.39 A cm⁻²) as compared to that on solid state deposited Cu-PDC cathode (-0.86 A cm⁻²) for the similar ratio of CO₂/H₂ ~ 75/25, which is possible due to the lower thickness of active cathode layer deposited by spray coating (400 nm) in comparison to the solid state deposited layer of Cu-PDC cathode (~40 μm). The thicker electrode could have large triple phase contact area and subsequently could offer higher area to commence electrochemical reduction of CO₂, leading to improve the reduction current.

सार

घनत्व कार्यात्मक सिद्धांत (डीएफटी) गणना सीरिया (110) सतह पर कार्बन डाइऑक्साइड (सीओ 2) को कार्बन मोनोऑक्साइड (सीओ) और मेथनॉल (सीएच 3 ओएच) में न्यूनीकरण के तंत्र का अध्ययन करने के लिए की जाती है। सीओ 2 को सीएच 3 ओएच में न्यूनीकरण के सुझाए गए मार्गों के लिए प्राथमिक कदमों की थर्मोकेमिस्ट्री का मूल्यांकन स्टॉइचियोमेट्रिक सेरिया सतह पर किया जाता है। गणना सबसे अनुकूल शोषण अभिविन्यास और प्रतिक्रिया मध्यवर्ती की संबंधित बाध्यकारी ऊर्जा निर्धारित करने के लिए की जाती है। कार्बोक्साइल (सीओओएच) या फॉर्मेट (एचसीओओ) मध्यवर्ती प्रजातियों के गठन के माध्यम से मैकेनिकल मार्गों पर विचार किया जाता है। कार्बोक्साइल ($\Delta E_{\text{बंधनकारी}} = -36.0$ केजे मोल⁻¹) की तुलना में स्टॉइकीओमिस्ट्री सीरिया की सतह पर, 222.9 केजे मोल⁻¹ की बाध्यकारी ऊर्जा के साथ फॉर्मेट अधिक स्थिर होने के लिए मनाया जाता है। फॉर्मेट प्रजातियां बाद के हाइड्रोजनीकरण पर एच H₂COOH उत्पादित की जाती है। मेथनॉल का उत्पादन करने के लिए, H₂COOH को H₂CO और OH में अलग करने की आवश्यकता होती है जो एक महत्वपूर्ण एंडोथर्मिक ($\Delta E_{\text{प्रतिक्रिया}} = 64.0$ केजे मोल⁻¹) चरण है। इसके विपरीत, कार्बोक्साइल इंटरमीडिएट से जुड़ा कुल मार्ग एक्सओथर्मिक है, जो सीओओ और ओएच (सीओएचएच → सीओ + ओएच) में सीओएचएच के विघटन को छोड़कर, 5.0 केजे मोल⁻¹ द्वारा एंडोथर्मिक है। कम सेरिया सतह पर, सीओ 2 ऑक्सीजन रिक्ति के साथ परस्पर क्रिया पर सीओ को अलग करता है। ऑक्सीजन परमाणु रिक्ति स्थल को ठीक करता है और क्रमशः 25 9.2 केजे मोल⁻¹ और 238 केजे मोल⁻¹ के आंतरिक सक्रियण और प्रतिक्रिया ऊर्जा के साथ एक रेडॉक्स तंत्र के माध्यम से स्टेचियोमेट्रिक सतह को पुनः उत्पन्न करता है। ऑक्सीजन रिक्तियों की पार्श्व परस्पर क्रिया का अध्ययन सीओओ 2 सतह की प्रति इकाई दो ऑक्सीजन रिक्तियों की पीढ़ी द्वारा किया जाता है। एक अलग रिक्ति की तुलना में, डी-रिक्ति पर सीओ 2 विघटन की सक्रियण और प्रतिक्रिया ऊर्जा लगभग अपने मूल्य के आधे से कम हो जाती है। न्यूनीकरण सतह पर हाइड्रोजन परमाणु सह- अधिशोषण करना एक कार्बोक्सिल इंटरमीडिएट, सीओ 2 + एच → सीओएचएच ($\Delta E_{\text{उत्प्रेरण}} = 39.0$ केजे मोल⁻¹, $\Delta E_{\text{एच}} = -69.2$ केजे मोल⁻¹) बनाकर सीओ 2 पृथक्करण में सहायता के लिए मनाया जाता है जो बाद में विघटन पर सीओ उत्पादन रेडॉक्स तंत्र के माध्यम से। हाइड्रोजनीकरण पर, सीओ से न्यूनीकरण से रेरिया सतह पर मेथनॉल का उत्पादन करने की संभावना है। मेथनॉल का उत्पादन करने के लिए सीओ हाइड्रोजनीकरण के ऊर्जावान ने सीयू (111) और सीओओ 2-एक्स / सीयू (111) इंटरफ़ेस के लिए रिपोर्ट की गई डीएफटी गणनाओं के मुकाबले सक्रियण बाधाओं के साथ असाधारण कदम दिखाए, जो दर्शाता है कि विस्तारित सीरिया की सतह सीओ 2 को सीओ और CH₃OH में न्यूनीकरण करने के लिए समान रूप से सक्रिय है। अलौकिक धातु कटियन (जीडी, एसएम और पीआर) के साथ सीरिया की सतह के आगे डोपिंग, फेशियल ऑक्सीजन रिक्ति निर्माण की सुविधा प्रदान कर सकती है और सीरिया जाली के अंदर इलेक्ट्रॉनिक और आयनिक चालकता में सुधार कर सकती है, जिससे सीओ 2 कमी प्रतिक्रिया के लिए इलेक्ट्रोकेटिटिक गतिविधि में वृद्धि होती है। 5-30% ($x = 0.05-0.3$) से डोपेंट एकाग्रता के विभिन्न स्तर के साथ शुद्ध सीरिया (सीओओ 2) और डोण्ड

सीरिया एमएक्ससी 1-एक्सओ 2-0.5x (एम = जीडी, एसएम और पीआर) में ऑक्सीजन आयन विसारकता निर्धारित करने के लिए आणविक गतिशील सिमुलेशन किए जाते हैं। जीडी के साथ डोपिंग ने अंडेण्ड सीरिया (डी = 1.33×10^{-10} सेमी² एस⁻¹ 1173 पर) की तुलना में परिमाण के दो क्रम (डी = 4.67×10^{-8} सेमी² एस⁻¹ 1173 के) द्वारा ऑक्सीजन आयन विसारक मूल्य में सुधार दिखाया। डोपिंग स्तर का 10% सभी डोपेंटों की इष्टतम एकाग्रता के रूप में अनुमान लगाया गया था, जिसमें सभी डोपेड सेरिया सामग्री ऑक्सीजन आयन की अधिकतम प्रसार दिखाती थीं। अध्ययन किए गए तीन डोपेंटों में से, पीआर 773-1173 के सिमुलेशन के तापमान सीमा में ऑक्सीजन आयन की अधिकतम प्रसार दिखाने के लिए मनाया गया था।

Gd_{0.1}Ce_{0.9}O_{2-δ} (जीडीसी) और Pr_{0.1}Ce_{0.9}O_{2-δ} (पीडीसी) का उपयोग करके तांबा के साथ कैथोड सामग्री के रूप में मिश्रित, ठोस ऑक्साइड कोशिकाओं को बना दिया जाता है। घुसपैठ तकनीक को उत्तेजित करने के लिए नियोजित किया जाता है: क्यू-जीडीसी और क्यू-पीडीसी इलेक्ट्रोड्स येट्रिया स्थिरीकृत ज़िकोनिया (वाईएसजेड) मचान में। घने वाईएसजेड चरण इलेक्ट्रोलाइट के रूप में प्रयोग किया जाता है और La_{0.8}Sr_{0.2}MnO_{3-δ} (एलएसएम) एसओईसी के एनोड के रूप में प्रयोग किया जाता है। सीयू-पीडीसी कैथोड के साथ सेल के ध्रुवीकरण प्रतिरोध को अपेक्षाकृत कम मूल्य 17.9 Ω सेमी² और 5.1 Ω सेमी² के रूप में मापा जाता है, जो सीओ 2 / एच 2 अनुपात के लिए सीयू-जीडीसी इलेक्ट्रोड पर संबंधित 23.8 Ω सेमी² और 7.5 Ω सेमी² की तुलना में मापा जाता है। क्रमशः / 08 और 28/82। इसी तरह, सीयू-पीडीसी कैथोड पर वर्तमान में सीओ 2 इलेक्ट्रोलिसिस को सीओ 2 / एच 2 = 76/24 पर -0.056 ए सेमी⁻² के मूल्यों के अपेक्षाकृत अधिक मापा जाता है, -0.069 सीओ 2 / एच 2 = 56/44 और -0.075 पर एक सेमी⁻² सीओ 2 / एच 2 = 38/62 पर एक सेमी⁻²। क्यू-पीडीसी कैथोड के इम्पैडेंस स्पेक्ट्रा को विभिन्न संभावित रूप से मापा जाता है, 17.9 Ω सेमी² से 6.3 Ω सेमी² तक ध्रुवीकरण प्रतिरोध में उल्लेखनीय कमी दर्शाती है क्योंकि लागू क्षमता ओसीवी (-0.8 9 वी) से -1.6 वी तक सीओ 2 / एच 2 = 92 पर बढ़ी है / 08। परिणामों ने सीयू-जीडीसी इलेक्ट्रोड की तुलना में क्यू-पीडीसी कैथोड की एक बेहतर इलेक्ट्रोकाटैटिक गतिविधि का सुझाव दिया। हालांकि घुसपैठ विधि द्वारा निर्मित सीयू-पीडीसी कैथोड के साथ सेल का इलेक्ट्रोकेमिकल प्रदर्शन, कम कमी वर्तमान तक सीमित है (-0.075 ए सेमी⁻² 2.0 वी पर)।

कैथोड इलेक्ट्रोकेटालिस्ट के रूपरेखा को संशोधित करने के लिए, फैब्रिकेशन तकनीक को बदल दिया गया है और ठोस ऑक्साइड सेल को क्यू-पीडीसी कैथोड, एलएसएम एनोड और वाईएसजेड के साथ इलेक्ट्रोलाइट के रूप में ठोस राज्य विधि का उपयोग करके तैयार किया जाता है। सीओ 2 / सीओ और सीओ 2 / एच 2 इलेक्ट्रोकेमिकल माप के विभिन्न वॉल्यूमेट्रिक अनुपात में लागू क्षमताओं को कम करने और पर्यावरण को कम करने के वातावरण को कम करने की भूमिका को समझने के लिए किया जाता है। सीओ-प्र 0.1ee.9.92-δ इलेक्ट्रोड का ध्रुवीकरण प्रतिरोध सीओ की वृद्धि के साथ 44.0 Ω सेमी² (सीओ 2 / सीओ = 9 3/07) से 7.0 Ω सेमी² (सीओ 2 / सीओ = 23/77) से घटने के लिए मनाया जाता है। एच 2 एकाग्रता में वृद्धि के साथ 7.5 Ω सेमी² (सीओ 2 / एच 2 = 9 7/03) से 1.0 Ω सेमी² (सीओ 2 / एच 2 = 24/76) के समान। सीओ

2 / एच 2 और सीओ 2 / सीओ के विभिन्न अनुपात पर, $-0.84 \text{ ए सेमी}^{-2}$ (वीएपी = 2.5 वी) और $-0.12 \text{ ए सेमी}^{-2}$ (वीएपी = 1.5 वी) की अधिकतम कमी वर्तमान 75/25 सीओ 2 / एच 2 और 93/07 सीओ 2 / सीओ क्रमशः। ठोस राज्य निर्मित सीयू-पीडीसी कैथोड ने घुमावदार सीयू-पीडीसी कैथोड ($-0.049 \text{ ए सेमी}^{-2}$ में 2.0 वी) की तुलना में 2.0 वी पर $-0.50 \text{ ए सेमी}^{-2}$ के उच्च कमी के साथ एक बेहतर इलेक्ट्रोकेमिकल प्रदर्शन दिखाया है। तापमान 1023 के सीओ 2 / एच 2 ($\sim 75/25$) के समान अनुपात 2.523 की सीओ उत्पादन के लिए सीओ उत्पादन के लिए दूरदराज के दक्षता के साथ 11% तक हासिल किया गया है (सीओ 2 / एच 2 अनुपात 75 / 25)।

स्प्रे पायरोलिसिस रणनीति घने YSZ सबस्ट्रेट पर पीडीसी आधारित कैथोड परत के घने चरण सूक्ष्म संरचना तैयार करने के लिए लागू होती है। घने पीडीसी पतली फिल्म (मोटाई $\sim 400 \text{ एनएम}$) पर, सीयू नाइट्रेट अग्रदूत इंजेक्शन और 673 के पर कैल्सीन किया जाता है। स्प्रे लेपित सीयू-पीडीसी कैथोड के साथ सेल का कुल ध्रुवीकरण प्रतिरोध अपेक्षाकृत कम ($7.10 \Omega \text{ सेमी}^{-2}$) है सीओ-पीडीसी ठोस राज्य ($7.90 \Omega \text{ सेमी}^{-2}$) और घुसपैठ तकनीक ($17.9 \Omega \text{ सेमी}^{-2}$) द्वारा सीओ 2 / एच 2 ($\sim 92/08$) के समान अनुपात के लिए 1023 के बराबर अनुपात के लिए निर्मित, स्प्रे लेपित पीडीसी का सुझाव देते हुए घने चरण सूक्ष्म संरचना, घुसपैठ और ठोस राज्य तैयार कैथोड घटक की तुलना में एक न्यूनतम चार्ज स्थानांतरण प्रतिरोध प्रदान करते हैं। हालांकि, 2.5 वी संभावित पर मापा गया अधिकतम कमी वर्तमान, ठोस राज्य जमा सीयू-पीडीसी कैथोड ($-0.86 \text{ ए सेमी}^{-2}$) की तुलना में स्प्रे जमा किए गए क्यू-पीडीसी कैथोड ($-0.39 \text{ ए सेमी}^{-2}$) के मामले में कम है।) सीओ 2 / एच 2 $\sim 75/25$ के समान अनुपात के लिए, जो सीयू-पीडीसी कैथोड (~ 40) की ठोस स्थिति जमा परत की तुलना में स्प्रे कोटिंग (400 एनएम) द्वारा जमा सक्रिय कैथोड परत की कम मोटाई के कारण संभव है (सूक्ष्ममापी)। मोटे इलेक्ट्रोड में बड़े ट्रिपल चरण संपर्क क्षेत्र हो सकते हैं और बाद में सीओ 2 की इलेक्ट्रोकेमिकल कमी शुरू करने के लिए उच्च क्षेत्र की पेशकश कर सकते हैं, जिससे वर्तमान में कमी में सुधार होता है।

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