KINETICS AND PERFORMANCE OF PEROVSKITE ANODES FOR METHANE ELECTROOXIDATION IN SOLID OXIDE FUEL CELLS

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THESIS CERTIFICATE

This is to certify that the thesis titled **Kinetics and Performance of Perovskite Anodes for Methane Electrooxidation in Solid Oxide Fuel Cell**, submitted by **U.N Mohamed Shahid**, to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**, is a bonafide record of the research work done by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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ABSTRACT

Perovskite anode materials with impregnated and doped electrocatalytic elements have been synthesized and tested in solid oxide fuel cells (SOFCs) to study their kinetics and performance for methane electrooxidation. In the initial stages, the efficient electrocatalyst combinations for methane electro-oxidation is studied. Various oxides like cerium oxide (CeO_2), cobalt oxide (Co_3O_4), iron oxide (Fe_3O_4) and copper oxide (CuO) were impregnated over the nickel cermet (N-Y) to yeild Ce-N-Y, Co-N-Y, Fe-N-Y and Cu-N-Y anodes. The kinetics of impregnated cermet anodes were studied using a three-electrode set up with an asymmetric reference electrode and the electrochemical rate constant, exchange current density (i_0) is estimated. The CeO_2-Ni and Co_3O_4-Ni combinations in Ce-N-Y and Co-N-Y anodes perform better compared to all other combinations with maximum power density of 436 mW cm^{-2} in CH_4. In the latter stages of the study, uni-doped ($La_{0.3}Sr_{0.5}TiO_{3-\delta}$, LST_{A-}) and bi-doped ($La_{0.3}Y_{0.1}Sr_{0.4}TiO_{3-\delta}$, $LYST_{A-}$) perovskites anodes are synthesized using solid state route and the oxide of nickel (Ni) is impregnated into the porous structure of full cells containing LST_{A-} and $LYST_{A-}$ anode using infiltration technique to yield (04)LST_{A-} and (04)$LYST_{A-}$ anodes. The kinetics of impregnated perovskite anodes, (04)LST_{A-} and (04)$LYST_{A-}$, were studied similar to impregnated cermet anodes and i_0 values are estimated. The i_0 values of (04)LST_{A-} and (04)$LYST_{A-}$ anodes were 25.3 mA cm^{-2} (8.9 mA cm^{-2}) and 20 mA cm^{-2} (7.5 mA cm^{-2}) in H_2 (CH_4). The obtained i_0 values were higher compared to traditional nickel cermet anodes of 3.1 mA cm^{-2} (1.8 mA cm^{-2}) in H_2 (CH_4). But, still the performance of (04)LST_{A-} and (04)$LYST_{A-}$ anodes were annihilated in CH_4 environment. To improve the performance in CH_4 environment, cerium oxide (CeO_2) is impregnated along with NiO to yield (84)LST_{A-} and (84)$LYST_{A-}$ anodes. The i_0 values of (84)LST_{A-} and (84)$LYST_{A-}$ anodes were 154.6 mA cm^{-2} (123.5 mA cm^{-2}) and 161.6 mA cm^{-2} (133.2 mA cm^{-2}) in H_2 (CH_4) which were higher compared to Ce-N-Y in H_2 (121.8 mA cm^{-2}) and CH_4 (83.3 mA cm^{-2}). The (84)LST_{A-} and (84)$LYST_{A-}$ anodes yielded a maximum power density of 490 mW cm^{-2} and 430 mW cm^{-2} which was higher compared to Ce-N-Y anode in CH_4. The impregnated perovskite anodes were also compared with doped perovskite anodes, $La_{0.3}Sr_{0.5}Ni_{0.04}Ti_{0.96}O_{3-\delta}$ ($LSN_{0.04}T_{A-}$), $La_{0.3}Sr_{0.5}Ni_{0.16}Ti_{0.84}O_{3-\delta}$ ($LSN_{0.16}T_{A-}$) and $La_{0.3}Y_{0.1}Sr_{0.4}Ni_{0.04}Ti_{0.96}O_{3-\delta}$ ($LYSN_{0.04}T_{A-}$) where the former outperformed the latter in terms of performance. The reasons for annihilated performance of doped perovskites were correlated to the structure-property relationship of the tailored perovskites. Finally, the improved performance of (84)LST_{A-} and (84)$LYST_{A-}$ anodes is attributed to the combination of mixed ionic and electronic conduction, oxygen vacancies in perovskite and induced metal support interactions between Ni-CeO_2 as observed using x-ray photoelectron spectroscopy, temperature programmed reduction and chemisorption studies. In addition, other physical characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscope, energy-dispersive analysis of X-ray spectroscopy, high resolution transmission electron microscope, Raman and photoluminescence spectroscopy were carried out to assess the phase purity, microstructure, constituent elements, carbon deposits and oxygen vacancies in tailored anodes, respectively.

KEYWORDS: Perovskite; Exchange current density; Kinetics; Methane .

सार

पेरोव्स्काइट एनोड मटिरियल तथा डोपेड इलेक्ट्रोकैटलिटिक एलीमेंट संश्लेषित किया गया तथासॉलिड ऑक्साइड फ़्यूल सेल्स (SOFCs) में मीथेन इलेक्ट्रोऑक्सीडेशन के लिए उनके कैनेटीक्स और प्रदर्शन का अध्ययन किया गया । प्रारंभिक चरणों में, एफ़्फ़ीसिएंट इलेक्ट्रोकेटालिस्ट के लिये मीथेन ऑक्सीकरण अध्ययन किया जाता है। विभिन्न ऑक्साइड जैसे सेरियम ऑक्साइड (CeO_2), कोबाल्ट ऑक्साइड (Co_3O_4), आयरन ऑक्साइड (Fe_3O_4) और कॉपर ऑक्साइड (CuO) को निकेल सेरमेट (N-Y) के ऊपर Ce-N-Y, Co-N-Y, Fe-N-Y और Cu-N-Y एनोड्स उत्पन्न करने के लिए लगाया गया था। इंप्रेग्नेटेड सेरमेट एनोड्स के कैनेटीक्स का अध्ययन एक तीन-इलेक्ट्रोड का उपयोग करके ए के साथ स्थापित। असममित संदर्भ इलेक्ट्रोड और विद्युत रासायनिक दर स्थिर, विनिमय धारा घनत्व (i_0) अनुमानित है । Ce-N-Y और Co-N-Y एनोड में CeO_2-Ni और Co_3O_4-Ni संयोजन CH_4 में 436 mW cm^{-2} की अधिकतम धारा घनत्व वाले अन्य सभी संयोजनों के लिए बेहतर प्रदर्शन करते हैं । अध्ययन के बाद के चरणों में, यूनी-डॉप्ड ($La_{0.3}Sr_{0.5}TiO_3$,LST_{A-}) और द्वि-डॉप्ड ($La_{0.3}Y_{0.1}Sr_{0.4}TiO_3$,$LYST_{A-}$) पर्कोव्साइट्स एनोड्स को सॉलिड स्टेट रूट का उपयोग करके संश्लेषित किया जाता है और निकेल (Ni) के ऑक्साइड को LST_{A-}और $LYST_{A-}$ एनोड युक्त पूर्ण कोशिकाओं की पोरस स्ट्रक्चर में इंफिल्ट्रेशन तकनीक का उपयोग करके (04)LST_{A-} और (04)$LYST_{A-}$ एनोड प्राप्त करने के लिए लगाया जाता है। इंप्रग्नेटेड पेरोव्स्काइट एनोड, (04)LST_{A-} और (04)$LYST_{A-}$ के कैनेटीक्स का अध्ययन इंप्रग्नेटेड सेरमेट एनोड के समान किया गया था और i_0 मानों का अनुमान लगाया गया है। (04)LST_{A-} और (04)$LYST_{A-}$ एनोड के i_0 मान H_2 (CH_4) में 25.3 mA cm^{-2} (8.9 mA cm^{-2}) और 20 mA cm^{-2} (7.5 mA cm^{-2}) थे । प्राप्त i_0 मान H_2 (CH_4) में 3.1 mA cm^{-2} (1.8 mA cm^{-2}) के पारंपरिक निकल सेरमेट एनोड की तुलना में अधिक थे। लेकिन, फिर भी (04)LST_{A-} और (04)$LYST_{A-}$ एनोड के प्रदर्शन को CH_4 वातावरण में नष्ट कर दिया गया। CH_4 वातावरण में प्रदर्शन को बेहतर बनाने के लिए, NiO के साथ सेरियम ऑक्साइड (CeO_2) को यील्ड (84)LST_{A-} और (84)$LYST_{A-}$ एनोड के लिए लगाया जाता है। (84)LST_{A-} और (84)$LYST_{A-}$ एनोड के i_0 मान H_2 (CH_4) में 154.6 mA cm^{-2} (123.5 mA cm^{-2}) और 161.6 mA cm^{-2} (133.2 mA cm^{-2}) थे जो H_2 (121.8 mA cm^{-2}) और CH4 (83.3 mA cm^{-2}) में Ce-NY की तुलना में अधिक थे । (84)LST_{A-} और (84)$LYST_{A-}$ एनोड्स ने 490 mW cm^{-2} और 430 mW cm^{-2} की अधिकतम धारा घनत्व प्राप्त किया जो CH_4 में Ce-N-Y एनोड की तुलना में अधिक था। इंप्रेग्नेटेड पेरोसाइट एनोड्स की तुलना डोप्ड पेरोसाइट एनोड्स, $La_{0.3}Sr_{0.5}Ni_{0.04}Ti_{0.96}O_{3-\delta}$ ($LSN_{0.04}T_{A-}$), $La_{0.3}Sr_{0.5}Ni_{0.16}Ti_{0.84}O_{3-\delta}$ ($LSN_{0.16}T_{A-}$), और $La_{0.3}Y_{0.1}Sr_{0.4}Ni_{0.04}Ti_{0.96}O_{3-\delta}$ ($LYSN_{0.04}T_{A-}$) जहां प्रदर्शन के मामले में पहले वाले ने बाद वाले से बेहतर प्रदर्शन किया। डोपेड पेरोव्स्काइट्स के एनीहिलटेड परफॉर्मेंस के कारणों को पेरोव्स्काइट्स की स्ट्रक्चर प्रॉपर्टि रेलेशनशिप सहसंबद्ध किया गया था । अंत में, (84)LST_{A-} और (84)$LYST_{A-}$ एनोड के बेहतर प्रदर्शन को मिश्रित आयनिक और इलेक्ट्रॉनिक चालन, पेरोसाइट में ऑक्सीजन वेकेंन्सीज़, और Ni-CeO_2 के बीच प्रेरित धातु समर्थन इंटरैक्शन के संयोजन के लिए जिम्मेदार ठहराया गया है, जैसा कि एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी, टेंपरेचर प्रोग्राम रिडेक्सिन, और केमीसोर्प्शिऑन स्टडीज़ का उपयोग करके देखा गया है। इसके अलावा, अन्य भौतिक लक्षण वर्णन तकनीक जैसे एक्स-रे विवर्तन (एक्सआरडी), फील्ड एमिस्सएन स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोप, एक्स-रे स्पेक्ट्रोस्कोपी का एनर्जि-डेस्पेर्सिव एनालिसिस, उच्च-रिज़ॉल्यूशन ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोप, रमन और फोटोल्यूमिनेशन स्पेक्ट्रोस्कोपी द्वारा क्रमशः फेज़ पूरिटी, माइक्रोस्ट्रक्चर, घटक तत्व, कार्बन डिपॉज़िटस और टेलर्ड एनोडस में ऑक्सीजन वेकेंन्सीज़ का आकलन करने के लिए किया गया था। ।

कीवर्ड: पेरोव्स्काइट; एक्स्चेंज करेंट डैन्सिटि; काइनेटिक्स; मीथेन

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ABBREVIATIONS

SOFC	Solid Oxide Fuel Cells
MIEC	Mixed Ionic and Electronic Conductor
OCV	Open Circuit Potential
FWHM	Full Width Half Maximum
X-RD	X-ray diffraction
SEM	Scanning Electron Microscope
FE-SEM	Field Emission-Scanning Electron Microscope
TEM	Transmission Electron Microscope
HR-TEM	High Resolution-Transmission Electron Microscope
XPS	X-ray Photoelectron Spectroscopy
TPR	Temperature Programmed Reduction
PL	Photoluminescence Spectroscopy
TEC	Thermal Expansion Coefficient
PSD	Particle Size Distribution
PMC	Particle Migration and Coalescence
OR	Ostwald Ripening
EIS	Electro-chemical Impedance Spectroscopy
LSV	Linear Sweep Voltammetry
HF	High Frequency
MF	Medium Frequency
LF	Low Frequency
NiO	Nickel Oxide
YSZ	Yttria Stabilized Zirconia
GDC	Gadolinium Doped Zirconia
LSM	Lanthanum Strontium Manganite
STO	Strontium Titanate
LST	Lanthanum Doped Strontium Titanate
YST	Yttrium Doped Strontium Titanate
STO$_{A-}$	A-site Deficient Strontium Titanate
LST$_{A-}$	A-site Deficient Lanthanum Doped Strontium Titanate

LYST$_{A-}$ A-site Deficient Lanthanum and Yttrium Doped Strontium Titanate

LSNT$_{A-}$ A-site Deficient Lanthanum and Nickel Doped Strontium Titanate

LCSNT$_{A-}$ A-site Deficient Lanthanum, Cerium and Nickel Doped Strontium Titanate

NOTATION

θ	Theta
I	Intensity, $a.u$
i	Current, mA
T	Temperature, ^0C
cm	Centimeters
μ	micron
i_o	Exchange Current Density, $mA\ cm^{-2}$
E_a	Activation Energy, $kJ\ mol^{-1}$
τ	Time Constant, s
f	Frequency, Hz
R	Resistance, Ω
$R^{'}$	Gas constant, $J\ mol^{-1}\ K^{-1}$
R_p	Polarization Resistance, Ω
C	Capacitance, F
η	Overpotential, V
V	Potential
W	Power
$Z^{'}$	Real Impedance, Ω
$Z^{"}$	Imaginary Impedance, Ω
β	Ramp rate, $^0C\ min^{-1}$
α	Alpha
A	Pre exponential factor