STUDY ON ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE TO SYNGAS

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by

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in fulfilment of the requirements of the degree of Doctor of Philosophy
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STATEMENT

I do hereby declare that this Ph.D. thesis entitled **"STUDY ON ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE TO SYNGAS"** is an original work carried out by me under the guidance and supervision of Prof. Anil Verma in the Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India and is submitted to Indian Institute of Technology Delhi, Hauz Khas, New Delhi, India, for the award of the degree of Doctor of Philosophy.

The interpretations put forth are based on my readings and understandings of the original text and are not submitted, in part or full, to any other university or institute for the award of any degree or diploma. I also certify that the details and information taken from the works of other investigators, articles and websites which I have made use of are acknowledged at the respective place in this thesis.

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CERTIFICATE

This is to certify that the work contained in this thesis entitled **"STUDY ON ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE TO SYNGAS"** submitted by Mr. Karan Malik to the Indian Institute of Technology Delhi, for the fulfilment of the requirements for the award of Doctor of Philosophy in Chemical Engineering is a record of bonafide research work carried out by him. I certify that he has carried out this work under my supervision. The research work is original, and this work has not been submitted elsewhere in part or full, to any other university or institute for the award of any degree or diploma. Also, the material obtained from other sources has been duly acknowledged in the thesis.

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(Karan Malik)

Abstract

Over the past few years, electrochemical reduction of CO_2 (ERC) has attracted a lot of interest among researchers to convert CO_2 into value added products using renewable energy. Through ERC, CO_2 and water using renewable energy, can be co-electrolyzed to produce many chemicals such as CH_4, C_2H_4, C_2H_6, HCOOH, CH_3OH, and syngas ($CO + H_2$), which are important industrial chemicals. However, CO_2 is a very stable molecule and thus it is very difficult to reduce it. Therefore, primary focus of research throughout the world has been on developing an electrocatalyst selective to CO_2 reduction. ERC is carried out in presence of water. Thermodynamically, the reduction potentials of ERC and hydrogen evolution reaction (HER) potential are close to each other. Moreover, HER has fast kinetics as compared to ERC. Thus, the electrical charge spent during ERC is used by the facile HER instead of ERC. Thus suppression of HER possess a huge challenge.

ERC can lead to many products i.e., CO, CH_4, C_2H_4, C_2H_6, HCOOH, and CH_3OH etc.; depending upon the electrode potential, electrolyte, electrocatalyst, and reaction conditions. Sixteen different products can be formed using Cu as electrocatalyst. However, it requires high overpotential (~1.0 V), have poor selectivity, and fast deactivation are biggest challenges. The research work in this thesis is focused on selective formation of syngas using Zn and Cu based electrocatalysts. Effect of nature of electrocatalyst layer on the ERC selectivity has been studied. It was found that degree of gas entrapped in different types of layers was different, leading to different selectivity. The role of addition of Cu into the ZnO has also been studied for the synthesis of syngas. On varying the concentration of Cu into the ZnO, it was found that at certain fraction of Cu into the ZnO, charge transfer resistance towards ERC is reduced which ultimately reduces the overpotential requirements. Role of pressure in gas phase ERC was also investigated. It was found that mild increase in pressure

leads to shift in Zn/Cu selectivity towards syngas formation. The knowledge gathered by the research work was disseminated through various research papers and presentations in various conferences.

Keywords: Electrochemical reduction of CO_2, Zn/Cu nanocomposite, Gas phase ERC, Elevated pressure.

सारांश

पिछले कुछ वर्षों में, कार्बन डाइऑक्साइड के विद्युत् रासायनिक परिवर्तन (ईआरसी) ने बहुत सारे शोधकर्ताओं मे इस रुचि को जगाया है की वह अक्षय ऊर्जा का उपयोग करके कार्बन डाइऑक्साइड को मूल्य वर्धित उत्पादो मे बदले | ईआरसी के दुवारा अक्षय ऊर्जा का उपयोग करते हुए कार्बन डाइऑक्साइड और जल को सह-इलेक्ट्रोलाइज करके अनेक रसायनो का उत्पादन किया जा सकता है | उदाहरण के लिए जेसै CH_4, C_2H_4, C_2H_6, HCOOH, CH_3OH, और सिंनगैस ($CO + H_2$) | येह सभी रसायन उद्योग-प्रधान के लिये बहुत महत्वपूर्ण है | लेकिन कार्बन डाइऑक्साइड एक बहुत ही स्थिर अणु है जिस्के करन कार्बन डाइऑक्साइड का विद्युत् रासायनिक परिवर्तन करना बहुत ही कठिन कर्य है | इसलिए दुनिय भर मे हो रहि शोध का प्राथमिक लक्ष्य एक ऐसे इलेक्ट्रोकैटेलिस्ट को बनाने मे है जोकि चयनित तरीकै से ईआरसी कर सके | ईआरसी को हमेशा जल की उपस्थिति मे ही किया जाता है | थर्मोडायनामिक रूप से ईआरसी का रीडकशन पोटेनशयल और हयढरोजन उत्पादन प्रतिक्रिया (अचईअर) के रीडकशन पोटेनशयल एक दुसरे के बहुत ही नज़दीक है | इसके अलावा ईआरसी के तुलनात्मक अचईअर के कैनेटीक्स बहुत ही तेज है | जिसके कारन, ईआरसी के दौरान खर्च किए गए विद्युत आवेश का उपयोग ईआरसी के बजाय सरल HER द्वारा किया जाता है। इस प्रकार ईआरसी का दमन एक बड़ी चुनौती है |

इलेक्ट्रोड क्षमता, इलेक्ट्रोलाइट, इलेक्ट्रोकैटलिस्ट और प्रतिक्रिया स्थितियों के आधार पर ईआरसी से कई उत्पाद जैसे CO, CH_4, C_2H_4, C_2H_6, HCOOH, और CH_3OH आदि बन सकते हैं। Cu का विद्युत उत्प्रेरक के रूप में उपयोग करके सोलह विभिन्न उत्पाद बनाए जा सकते हैं। हालाँकि, इसके लिए जरूरी उच्च विद्युत् क्षमता (~ 1.0 V) की आवश्यकता, खराब चयनशीलता और इस्की तेजी से निष्क्रियता सबसे बड़ी चुनौतियाँ होती हैं। इस थीसिस में शोध कार्य Zn और Cu आधारित

इलेक्ट्रोकैटेलिस का उपयोग करके सिंनगैस के चयनात्मक गठन पर केंद्रित है | ईआरसी की चयनशीलता पर इलेक्ट्रोकैटेलिस्ट की परत की प्रकृति के प्रभाव का अध्ययन किया गया है। यह पाया गया कि विभिन प्रकार की परतों में फंसी गैस की मात्रा अलग थी, जिससे अलग अलग चयनशीलता होती है । सिंनगैस के संश्लेषण के लिए Cu को Zn में जोडने की भूमिका का भी अध्ययन किया गया है। Zn में Cu की एकाग्रता को अलग करने पर, यह पाया गया कि Zn में Cu के कुछ अंश पर, ईआरसी के प्रति चार्ज ट्रांसफर प्रतिरोध कम हो जाता है जो अंततः अतिपौतापूर्ण आवश्यकताओं को कम करता है। गैस फेज ईआरसी में दबाव की भूमिका की भी अध्ययन किया गया है । इस दोरान यह पाया गया कि दबाव में हल्की वृद्धि से Zn/Cu की चयनता सिंनगैस के गठन की दिशा में बढती है । शोध कार्य से एकत्रित ज्ञान को विभिन सम्मेलनों में विभिन शोध पत्रों व प्रस्तुतियों के माध्यम से प्रसारित किया गया।

कीवर्ड: कार्बन डाइऑक्साइड के विद्युत् रासायनिक परिवर्तन, Zn/Cu नैनोकंपोसाइट, गैस चरण ईआरसी, उच्च दबाव |

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List of Abbreviations

ACL	Anode catalyst layer
AEM	Anion exchange membrane
AGDL	Anode gas diffusion layer
BET	Brunauer–Emmett–Teller
BMT	Billion metric ton
BP	British petroleum
CCL	Cathode catalyst layer
CEA	Central electricity authority
CGDL	Cathode gas diffusion layer
CF	Carbon fibre
CL	Catalyst layer
CPE	Constant phase element
CV	Cyclic voltammetry
DFT	Density functional theory
DI	De-ionized
DME	Dimethyl ether
ECSA	Electrochemically active surface area
EDX	Energy dispersive X-ray spectroscopy
EIS	Electrochemical Impedance spectroscopy
EPR	Electron paramagnetic resonance
ERC	Electrochemical reduction of CO_2
FE	Faradaic efficiency
FESEM	Field emission scanning electron microscopy
FID	Flame ionization detector

FTIR	Fourier transform infrared
FWHM	Full-width-at-half-maxima
GA	Glutaraldehyde
GC	Gas chromatography
GCE	Glassy carbon electrode
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
HER	Hydrogen electrode potential
HRTEM	High resolution transmission electron microscopy
IPCC	International panel on climate change
L/D	Length/diameter
LSV	Linear sweep voltammetry
MEA	Membrane electrode assembly
MFC	Mass flow controller
MPL	Micro porous layer
MWCNT	Multiwall carbon nano tubes
NHE	Normal hydrogen electrode
OCP	Open circuit potential
OELM	Online electrochemical mass spectroscopy
PEI	Polyethyleneimine
PL	Photoluminescence
PPM	Parts per million
PTFE	Poly-tetrafluoroethylene
PVA	Poly-vinyl alcohol
QPEI	Quaternized polyethyleneimine
RDS	Rate determining step

Rh	Relative humidity
RHE	Reversible hydrogen electrode
SEM	Scanning electron microscopy
SIFT-MS	Selected ion flow tube mass spectrometry
SOFC	Solid oxide fuel cell
SPE	Solid polymer electrolyte
STP	Standard temperature and pressure
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

List of Nomenclatures

b	Width of the channel (m)
β	Ratio of the CO_2 left after the CO_2-H_2O and CO_2-OH^- reactions to the total dissolved CO_2 (-)
β_1	Ratio of the CO_2 flux onto the electrocatalyst surface to the total CO_2 flux through the CGDL (-)
$C_{CO_2,ch}$	CO_2 concentration in channel (M)
$C_{H_2O,ch}$	H_2O concentration in the channel (M)
d	Spacing between two crystal planes (nm)
$D_{A\text{-}aq}$	Diffusivity coefficient of species 'A' diffusing in liquid phase (m^2/s)
D_{AB}	Diffusivity coefficient of species 'A' diffusing through species 'B' in in gas phase (m^2/s)
D_{AB}^{eff}	Effective diffusivity coefficient of species 'A' diffusing through species 'B' in gas phase (m^2/s)
E°	Standard reduction potential (V)
ε_A, ε_B	Gas force constant (-)
ΔG_f°	Change in Gibbs free energy of formation at STP (kJ/mol)
ΔG_{rxn}°	Change in Gibbs free energy of reaction at STP (kJ/mol)
F	Faraday constant (C/mol)
FE_{CO}	CO Faradaic efficiency (%)
FE_{H_2}	H_2 Faradaic efficiency (%)
FE_{CH_4}	Methane Faradaic efficiency (%)
$FE_{C_2H_4}$	Ethene Faradaic efficiency (%)
$FE_{C_2H_6}$	Ethane Faradaic efficiency (%)
FE_{CH_3OH}	Methanol Faradaic efficiency (%)
$FE_{C_2H_5OH}$	Ethanol Faradaic efficiency (%)
$H_{CO_2,aq}$	Henry's constant for CO_2 (atm/M)

J_{CO}	CO partial current density (mA/cm^2)
J_0	Exchange current density (mA/cm^2)
L	Channel length (m)
L_g	Diffusion length in the GDL (μm)
L_l	Diffusion length in the liquid layer (μm)
M_A	Molecular weight of the species 'A' (kg/mol)
M_B	Molecular weight of the species 'B' (kg/mol)
n	Number of moles of electrons required to form 1 mole of reaction product (-)
$N_{GDL}^{CO_2}$	CO_2 flux through CGDL (mol/cm^2-s)
N_{cl}^{i}	Flux of species 'i' through the CCL (mol/cm^2-s)
p_t	Absolute pressure (N/m^2)
Q_{tot}	Total charge passed (C)
R_{ct}	Charge transfer resistance (Ω)
R_e	Electrolyte resistance (Ω)
θ	Bragg's angle (°)
λ	Wavelength of the incident X-rays (Å)
η_{act}	Activation overpotential (V)
η_{nerst}	Concentration overpotential (V)
∅	GDL porosity (-)
V_{ch}	Average velocity in the channel (m/s)
z	Moles of a particular product formed (mol)
ϑ_A	Solute molar volume at the normal boiling point (m^3/kmol)
φ	Association factor for solvent (-)
μ	Viscosity (kg/m-s)