Micro Surface Discharge for Plasma-Assisted Catalysis in Portable Fuel Cell Reforming Applications

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Preface

This dissertation is based on my research completed during my time as a research assistant at the Institute for Microtechnology at the Technische Universität Braunschweig, from February 2008 until the spring of 2012.

Firstly, I would like to thank my advisor Prof. Dr. S. Büttgenbach, head of the Institute for Microtechnology during the majority of my time there. The availability of excellent facilities, as well as a wonderful working atmosphere presented an outstanding environment in which to conduct the presented scientific work. I would also like to thank Prof. K.-H. Gericke, head of the Division of Laser Chemistry at the Institute for Physical Chemistry, for his acceptance of the co-examiner role in the examination committee. Through the help and cooperation of his research group this work was made possible. Thanks are also due to Prof. A. Dietzel, who, as of the spring of 2012, has taken over responsibility as the head of the Institute for Microtechnology and was willing to act as the chairperson of the examination committee. I wish him all the best in leading the IMT in the future.

Further, I would like to thank both the Bundesministerium für Bildung und Forschung and the Volkswagen Stiftung for their generous funding of the MIMEMIZ and P3M projects, respectfully. Through their support, new findings and discoveries were possible that led to this work.

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Symbols

A	Area	m^2
b	Tafel slope	V
c	Speed of light ($=3\cdot10^8$)	$m\cdot s^{-1}$
C	Capacitance	F
C	Concentration	m^{-3}
d	Thickness	m
D	Diameter	m
e	Elementary charge, ($=1.602\cdot10^{-16}$)	C
E	Electric field strength	$V\cdot m^{-1}$
E	Electric potential	V
F	Faraday constant, (=96,485)	$C\cdot mol^{-1}$
G	Gibb's free energy	$J\cdot mol^{-1}$
h	Planck constant, ($=4.135\cdot10^{15}$)	$eV\cdot s$
H	Enthalpy	$J\cdot mol^{-1}$
i	Current	A
I	Intensity	-
j	Current density	$A\cdot m^{-2}$
k_B	Boltzmann constant, ($=8.617\cdot10^{-5}$)	$eV\cdot K^{-1}$
m_e	Electron mass ($=9.11\cdot10^{-31}$)	kg
m_i	Ion mass	kg
n_e	Electron density	m^{-3}
n_g	Neutral gas density	m^{-3}
n_i	Ion density	m^{-3}
p	Partial pressure	Pa
p	Pressure	Pa
Q	Heat	J
R	Resistance	Ohm
R	Universal gas constant	$J\cdot K^{-1}\cdot mol^{-1}$
S	Entropy	$J\cdot K^{-1}\cdot mol^{-1}$
T	Temperature	K
v	Velocity	$m\cdot s^{-1}$
	Volume	m^3
W	Work	J
z	Position	m
Z	Charge state	-
α	Degree of ionization	-
α	Ionization coefficient	-
β	Charge transfer coefficient	-
γ	Secondary ionization coefficient	-
ε_0	Permittivity of free space, ($=8.85\cdot10^{-12}$)	$F\cdot m^{-1}$
ϵ	Energy	eV
η	Efficiency	-
κ	Electrical conductivity	$S\cdot m^{-1}$
λ	Wavelength	m
λ_D	Debye shielding radius	m
λ_e	Electron mean free path	m
ρ	Density	$kg\cdot m^3$
μ	Permeability of free space, ($=4\pi\cdot10^7$)	$V\cdot s\cdot A^{-1}\cdot m^{-1}$
μ	Dynamic viscosity	$Pa\cdot s$
σ	Collisional cross section	m^2
ω_{pe}	Electron plasma frequency	$rad\cdot s^{-1}$
ω_{pi}	Ion plasma frequency	$rad\cdot s^{-1}$

Kurzfassung

Die Erzeugung eines Nichtgleichgewichtsplasmas bei Atmosphärendruck zeigt immer wieder Vorteile bei Niedertemperatur-Anwendungen und erlaubt den Betrieb, wo Vakuumanlagen nicht realisierbar sind. Mikroplasmen, Nichtgleichgewichtsplasmen in Geometrien von weniger als einem Millimeter, haben insbesondere gute Eigenschaften hinsichtlich der homogenen chemischen Reaktion und des niedrigen Leistungsbedarfes, so dass sie für portable Anwendungen geeignet sind.

In dieser Arbeit wird das neuartige Design eines Barrierenentladungsreaktors, genauer eines sogenannten Mikrooberflächenentladungsreaktors (MSD), für die Anwendung in plasmaunterstützten katalytischen Brennstoffreformern präsentiert, um in einer Hochtemperatur (HT) Polymer-Elektrolyt-Membran-Brennstoffzelle eingesetzt zu werden. Die Erzeugung von hohen elektrischen Feldern, die für die Entladung benötigt werden, wurde simuliert und die einzelnen Komponenten analytisch betrachtet.

Durch Anwendung von mikrotechnologischen Prozessen wurde die monolithische Kombination elektrischer und fluidischer Komponenten realisiert. Die praktische Machbarkeit des Reaktors wurde während der Auslegung berücksichtigt, mit einem Fokus auf der Integration in eine Brennstoffzelle und minimalem Volumen. Dieses war abhängig von der Anpassung des Reaktors an die kleinsten industriell verfügbaren Generatorkomponenten. Um die Entladungs- und Plasmaeigenschaften zu charakterisieren, wurde der Reaktor optisch, elektrisch und thermisch analysiert.

Die Verwendung des MSD Reaktors wurde für die Reformierung von Methan in Wasserstoff für Brennstoffzellenanwendungen untersucht. Dazu wurde ein spezielles Gehäuse angefertigt, um den mikrostrukturierten Reaktor mit pneumatischen und elektrischen Makroverbindungen zu verschließen. Die Umsatzrate, die Produktselektivität und der Wirkungsgrad der Reaktion wurde für unterschiedliche Durchflussraten des Edukts, dessen Zusammensetzung, sowie bei Anwesenheit eines heterogenen Katalysators, bei verschiedenen Plasmaleistungen durchgeführt. Der wesentliche Umsatz des Methans, sowie thermische, mechanische und chemische Beständigkeit des Reaktors wurden demonstriert. Besonders wurde ein synergistischer Effekt entdeckt, wobei sich die Bildung von Wasserstoff signifikant steigerte, bei der Verwendung einer Kombination von Plasma und einem Katalysator gegenüber dem Betrieb ohne.

Zukünftige Versuche mit anderen Brennstoffen und bei erhöhter Temperatur könnten zu einer Weiterentwicklung führen und einen Beweis für die Umsetzbarkeit des Reaktors liefern. Diese Fallstudie zeigt, dass derartige Reaktoren ein großes Potential für portable Leistungsquellen haben. Es handelt sich bei den untersuchten Reaktoren um die den ersten miniaturisierten, portablen Reaktoren. Die Ergebnisse dieser Arbeit sollen als Basis für weitere Forschung dienen.

Abstract

The production of non-equilibrium plasma at atmospheric pressure has and continues to prove advantageous for low-temperature applications where use of vacuum pumps is not feasible. Microplasmas, plasma generated in sub-millimeter dimensions, have proven capable of producing such characteristics for homogeneous chemical reactions and, as of late, have been designed to allow a portable operation with low power requirements.

In this work, the novel design and application of a barrier type electrical discharge reactor, a so called micro surface discharge (MSD) reactor, is presented for application in plasma-assisted catalytic fuel reformation for a portable High-Temperature (HT) Polymer Electrolyte Membrane Fuel Cell (PEMFC). The reactor is optimized for temperature durability and leak tightness based on material choice and geometry. The generation of the high electric fields needed for electrical breakdown were simulated and analytically contemplated.

Using micro-technological processes, the combination of electrical and fluidic components was realized monolithically. The practical feasibility of the device was strongly taken into consideration, with focus on the device-fuel cell integration and minimal reactor volume, which was dependent on the adjustment of the reactor design with respect to the smallest industrially available generator components. The reactor was optically, electrically and thermally analyzed in order to characterize the breakdown mode and plasma properties.

The use of the MSD reactor for the reformation of methane into hydrogen for application in fuel cells was investigated, using a purpose built enclosure to connect the micro-structured reactor to various macroscopic interfaces, such as standard pneumatic and electrical connections. The conversion rate, product selectivity and reaction efficiency were examined with varying flow rates, inlet gas compositions, heterogeneous catalyst presence and plasma power loads. Significant methane conversion, as well as thermal, mechanical and chemical durability of the reactor was observed. Specifically, a synergistic effect was discovered where the production of hydrogen was significantly higher with a combination of plasma and catalyst than the addition of their productions separately.

Future experiments with other fuels and at elevated temperatures could continue to develop and prove the feasibility of this reactor in portable reforming applications. This case study has proven significant potential for portable power generation applications and is the first truly miniaturized portable reactor optimized for such applications. The results from this work should serve as a basis for further research of even more compact systems with even higher efficiency.

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