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Peter Kúš

Thin-Film Catalysts for Proton Exchange Membrane Water Electrolyzers and Unitized Regenerative Fuel Cells

Doctoral Thesis accepted by
the Charles University, Prague, Czech Republic

Springer

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ISSN 2190-5053 ISSN 2190-5061 (electronic)
Springer Theses
ISBN 978-3-030-20858-5 ISBN 978-3-030-20859-2 (eBook)
https://doi.org/10.1007/978-3-030-20859-2

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Supervisor's Foreword

Modern society is, more than ever before, relying on a constant supply of large amount of energy. At the same time, significant public pressure is put on leading governments and industry to strengthen the shift from fossil fuels to renewable sources. The full-scale transition to renewable energy is, however, not possible without resolving certain issues. Since it is fair to expect that major part of produced energy will come from volatile sources (e.g., solar and wind), it is necessary to have a reliable and scalable way of storing and releasing it in order to meet the demands of consumers. One of the possible solutions is the implementation of hydrogen economy. The idea is that overproduced electricity would be electrochemically converted to gaseous hydrogen and oxygen via water electrolysis; generated hydrogen could be either injected into the existing natural gas pipeline, used as fuel for H_2-powered vehicles or be stored and eventually, when needed, turned back to electricity through fuel cells. The most suitable electrochemical devices for above-mentioned conversions are the proton exchange membrane water electrolyzers and fuel cells. Wider commercialization of these systems is, however, hindered by their dependence on noble metal catalysts.

In his dissertation thesis, Dr. Peter Kúš provides very deep yet comprehensive insight into the concept of hydrogen economy and approaches the problem of lowering the noble metal loading from several directions. First part of the work investigates the possibility of using magnetron sputtering for deposition of iridium onto the anode side of water electrolyzer. Although the oxygen evolution reaction which runs on the anode is exceptionally catalyst-demanding, the systematic investigation resulted in design of a unique thin-film Ir/TiC structure which performed comparable to the state-of-the-art catalysts despite utilizing just a fraction of their noble metal loading. Second part of the thesis revolves around the idea of merging the electrolyzer and fuel cell into one bifunctional system—the unitized regenerative fuel cell. This approach is convenient in applications where the complete cycle of electricity $\rightarrow H_2 \rightarrow$ electricity takes place and might lead to significant savings in catalysts, since the amount of electrodes is effectively reduced to half. Wide arsenal of analytical techniques ranging from photoelectron spectroscopy to electrochemical atomic force microscopy helped to identify and

consequently address the crucial aspects which influence the performance of the bifunctional catalyst in both operational regimes. The optimized sandwich-like thin-film Ir/TiC/Pt anode catalyst yielded exceptional performance considering its very low noble metal loading.

Peter's thesis can be conceptually placed somewhere between research and application. That being said, I believe that the know-how gained from his systematic reasoning combined with "trial-and-error" approach will prove to be equally valuable as the experimental results themselves. His work might serve as a solid introductory material for students getting acquainted with the topic as well as an experimental guideline for more experienced researchers.

Prague, Czech Republic
March 2019

Prof. Vladimír Matolín

Abstract

This dissertation thesis revolves around hydrogen economy and energy-storage electrochemical systems. More specifically, it investigates the possibility of using magnetron sputtering for deposition of efficient thin-film anode catalysts with low noble metal content for proton exchange membrane water electrolyzers (PEM-WEs) and unitized regenerative fuel cells (PEM-URFCs). The motivation for this research derives from the urgent need of minimizing the price of mentioned electrochemical devices should they enter mass production.

Numerous experiments were carried out, correlating the actual in-cell performance with the varying position of thin-film catalyst within the membrane electrode assembly, with the composition of high-surface support sublayer, and with the chemical structure of the catalyst itself. The wide arsenal of analytical methods ranging from electrochemical impedance spectroscopy through scanning electron microscopy to photoelectron spectroscopy allowed us to describe complex phenomena behind different obtained efficiencies. Consequent systematic optimizations led to the design of novel PEM-WE anode thin-film iridium catalyst with thickness of just 50 nm, supported on optimized TiC-based sublayer which performed similarly to standard counterparts despite using just a fraction of their noble metal content. Moreover, the novel anode thin-film bifunctional Ir/TiC/Pt sandwich-like PEM-URFC catalyst yielded 31.15% round-trip efficiency in comparison to 40.02% given by a combination of dedicated high-loading devices.

Keywords Hydrogen economy · PEM water electrolyzer · PEM unitized regenerative fuel cell · Thin-film deposition · Low-loading catalyst

Acknowledgements

To this day, I have spent nearly seven years at the Department of Surface and Plasma Science. During this time, I have learned from and worked along very inspiring people, many of whom have become my dear and respected friends. There was always someone to help me, and I never had to ask for advice twice.

First and foremost, I would like to thank my supervisor Prof. Matolín, who introduced me to the topic, led me for the entire duration of my studies, and gave me a chance to cooperate with researchers worldwide on the international level.

Secondly, I want to thank Assoc. Prof. Matolínová for many valuable comments and recommendations regarding my work.

Special thanks to Dr. Fiala and Dr. Václavů, who knew the answer to every one of my complex questions and always pushed me in the right direction.

Next, I want to thank Dr. Ostroverkh for aiding me with MEA setup and for carrying out the fuel cell measurements.

I would also like to thank Dr. Khalakhan for his invaluable assistance during CERIC experiments and electrochemistry-related issues.

Many thanks to Dr. Kettner, Dr. Duchoň, and other colleagues from the Surface Physics Group and Nanomaterials Group who helped me countless times not only in scientific but also in personal matters.

Last but not least, a huge thanks to my parents, girlfriend, and friends outside of the academia, who kept supporting me no matter what and always fueled me with positive energy.

This work was supported by CERIC Consortium and Grant Agency of the Charles University, Projects No. 236214 and No. 1016217.

Prague, Czech Republic — Dr. Peter Kúš
July 2018

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Abbreviations

AFM	Atomic force microscopy
BE	Binding energy
BSE	Backscattered electrons
CCM	Catalyst-coated membrane
EDX	Energy-dispersive X-ray spectroscopy
FC	Fuel cell
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
HER	Hydrogen evolution reaction
HHV	Higher heating value
HOPG	Highly oriented pyrolytic graphite
HOR	Hydrogen oxidation reaction
IMFP	Inelastic mean free path
ITO	Indium tin oxide
LHV	Lower heating value
LOHC	Liquid organic hydrogen carrier
MEA	Membrane electrode assembly
OER	Oxygen evolution reaction
ORR	Oxygen reduction reaction
PEIS	Potentiostatic electrochemical impedance spectroscopy
PEM	Proton exchange membrane
PEM-FC	Proton exchange membrane fuel cell
PEM-URFC	Proton exchange membrane unitized regenerative fuel cell
PEM-WE	Proton exchange membrane water electrolyzer
PES	Photoelectron spectroscopy
PTFE	Polytetrafluoroethylene (i.e., Teflon)
PVD	Physical vapor deposition
RSF	Relative sensitivity factor
SE	Secondary electrons
SEM	Scanning electron microscopy

SHE	Standard hydrogen electrode
SRPES	Synchrotron radiation photoelectron spectroscopy
STP	Standard temperature and pressure
TFE	Tetrafluoroethylene
TPB	Triple-phase boundary
URFC	Unitized regenerative fuel cell
WE	Water electrolyzer
XPS	X-ray photoelectron spectroscopy