Probing the electronic properties of nickel(II) oxide (NiO) as electrocatalysts for renewable and sustainable electrolytic hydrogen production

Cobus Kriek (NWU), Frode Seland (NTNU)
Anzel Falch (NWU), Svein Sunde (NTNU), Bruno Pollet (NTNU)

South Africa – Norway Cooperation on Ocean Research, Including Blue Economy, Climate Change and Sustainable Energy (SANOCEAN)

– Launching Conference, 25 - 27 March 2019 –
Øystein Ulleberg
Principal Scientist – Institute for Energy Technology (Norway)
Renewable Energy Systems / Hydrogen Systems

1. Through joint contact (Dr. Øystein Ulleberg)
   - Dr. Ulleberg is leading a Norwegian research center (FME) on Zero Emission Energy Systems for Transport (MoZEEs)
   - Prof. Seland and Sunde are active participants in the FME
   - After contact made by Prof Kriek, Ulleberg (who knew Prof. Kriek from his time in South Africa) put us in contact early March 2018

2. Mutual scientific interest
   - Led to joint application to Sanocean
   - Prof. Pollet joined the group with his significant experience and interest in Hydrogen electrochemistry and strong connections to South Africa
A Few Facts on Hydrogen

- It is the simplest and lightest of all elements
- It makes up about 75% of the universe’s mass
- No hydrogen – no life!
  - The sun burns hydrogen
  - Present in all vegetable and animal tissue … and water (H₂O)
- From the Greek word meaning ‘water forming’
Decentralised hydrogen production (DH$_2$P):
Energy conversion & storage, for backup power and fuel cell electric vehicles (FCEV).
Hydrogen Refueling Stations

- > 250 currently
- > 1000 over the next five years

https://www.iea.org/tcep/energyintegration/hydrogen/
Hydrogen Research @ NTNU

https://www.ntnu.edu/energy/hydrogen
Electrochemistry at NTNU

https://www.ntnu.edu/ima/research/electrochemistry

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Department of Energy and Process Engineering, DEPE
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Odne S. Burheim    Håvard Karoliussen    Bruno G. Pollet
Some active projects

- Oxygen evolution at DSA electrodes in sulphate based electrolytes (SUPREME)
- Hydrogen Production by Alkaline Polymer Electrolyte Electrolysis (HAPEEL)
- Next Generation Electrodes for Anion Exchange Membrane Fuel Cells (NEXTGAME)
- Oxygen evolution on nanostructured Ni in alkaline solution (Strategic grant with DTU)
- Low cost bipolar plates for alkaline water electrolysis (MoZEES)
- Collaboration with Canadian Network, NiElectroCan
- Probing the electronic properties of (NiO) as electrocatalyst for hydrogen production (Sanocean)
- Bipolar plates for fuel cells
- Advanced rotating water electrolysis
Selected Equipment and Facilities (NTNU/SINTEF)

- Potentiostats/galvanostats
- Photoelectrochemistry
- Sonoelectrochemistry
- Electrochemical FTIR and Raman
- Electrochemical AFM/STM
- UV-vis PMRS
- Microfluidic flow cells
- Advanced electrochemical equipment (R(R)DE, DEIS, DEMS, EQCM)
- Battery/fuel cell/water electrolyzer test stations
- Ultrasonic devices (baths, probes & US-spray)
- Glove boxes, etc
- Clean room facility (NTNU NanoLab)
- SEM, XRD, XPS, TEM

NTNU NanoLab

€30m

Leadership or partner in several National Infrastructures [NorFAB (NanoLab), NorTEM, RECX, MiMAC, Solar and Hydrogen and fuel cells]
In order to strengthen and increase fuel cell and electrolyser research activities at SINTEFs/NTNUs new equipment have been installed & commissioned

- **PEM/AEM fuel cell and electrolyser test stations** 400-500 W
- **DMFC fuel cell test station** 40W
- **PEM fuel cell and electrolyser stack test stations** 10-12 kW
- **SOFC/SOEC** 650 W & 6 kW
Electrochemistry at NWU

Cobus Kriek
Anzel Falch
Electrochemistry Related Projects at NWU

\[ \text{SO}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{Catalyst}} \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \]

SO\textsubscript{2} electro-oxidation reaction (SO\textsubscript{2} EOR)

\[ \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2\text{H}_2 \]

Photocatalytic reduction of dissolved PGMs

\[ [\text{PdCl}_4]^{2-} \rightarrow \text{Pd}(s) + 4\text{Cl}^- \]

Pd(aq) + Sun → Pd(s)
Electrochemistry Related Projects at NWU

\[ 2\text{H}_2\text{O} + \text{Cat} \rightarrow 2\text{H}_2 + \text{O}_2 \]

\[ 4\text{OH}^- + \text{Cat} \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \]

Oxygen evolution reaction (OER)

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]

Oxygen reduction reaction (ORR)

\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{Cat} \]
Electrochemistry Related Projects at NWU

\[ 2H_2O + \overset{-}{\text{-}} \overset{+}{+} \rightarrow 2H_2 + O_2 \]

\[ 4OH^- \overset{\text{Catalyst}}{\rightarrow} O_2 + 2H_2O + 4e^- \]

Oxygen evolution reaction (OER)

\[ 2H_2O + \overset{-}{\text{-}} \overset{+}{+} \overset{\text{ sunlight}}{\rightarrow} 2H_2 + O_2 \]
Electrochemistry Related Equipment at NWU

- Potentiostats – single, bi and 64-channel
- RDE, RRDE
- Electrochemical Quartz Crystal Microbalance
- Spincoating
- Physical Vapour Deposition (PVD) / Sputtering
- Combinatorial PVD Screening
- Rapid Thermal Annealing
- UV-VIS Spectrophotometry
- Photocatalysis
- Photo-electrocatalysis
- SEM, TEM
Splitting water is NOT spontaneous

\[ 2H_2O + 285.8 \text{ kJ/mol} \rightarrow 2H_2 + O_2 \]
2H₂O → 2H₂ + O₂

Energy barrier is reduced by a catalyst

Uphill reaction
Introduction

△ H₂ Production Rate □ Electrocatalyst PGM Content ○ Aggressive Environment

Negative

Positive

High

Low

△ □ ○

Pt, IrO₂, RuO₂

Fe/NiO

Alkaline Water Electrolysis

Improved Alkaline Water Electrolysis

Acidic Water Electrolysis
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Ni(II) Oxide (NiO) as Electrocatalyst for Alkaline Electrolysis

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Synthesis Method</th>
<th>Overpotential/mV (at 10 mA.cm⁻²)</th>
<th>Electrolyte/M KOH</th>
<th>Reference</th>
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<tbody>
<tr>
<td>NiO nanoparticles</td>
<td>Citrate sol-gel</td>
<td>263</td>
<td>0.1</td>
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<tr>
<td>NiOₓ thin film</td>
<td>Hydrothermal</td>
<td>&gt;300 (at 1 mA.cm⁻²)</td>
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<td>NiOₓ bulk/film</td>
<td>Electrodeposition</td>
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<td>1.0</td>
<td>[22]</td>
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<tr>
<td>NiO nanoparticles</td>
<td>Obtained from Aldrich</td>
<td>331</td>
<td>1.0</td>
<td>[22]</td>
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<tr>
<td>NiO nanowires</td>
<td>Solvothermal</td>
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<td>0.5</td>
<td>[21]</td>
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<tr>
<td>NiO nanorods</td>
<td>Hydrothermal</td>
<td>364</td>
<td>1.0</td>
<td>[20]</td>
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<tr>
<td>NiOₓ</td>
<td>Electrodeposition</td>
<td>&gt;400</td>
<td>1.0 (NaOH)</td>
<td>[26]</td>
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<tr>
<td>NiO nanoparticles</td>
<td>Hydrothermal</td>
<td>409</td>
<td>0.5</td>
<td>[16]</td>
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<tr>
<td>NiO nanosheets</td>
<td>Hydrothermal</td>
<td>422</td>
<td>0.1</td>
<td>[17]</td>
</tr>
</tbody>
</table>

FeₓNi₁₋ₓO
(Iron doped Nickel Oxide)

RuO₂ (380 mV); IrO₂ (380 mV); IrO₂ (320 mV):
As early as 1987 the catalysis of the OER by Fe impurities in thin film nickel oxide (NiO) electrodes have been reported by Corrigan *

in a ‘viewpoint’ paper, Trotochaud and Boettcher commented that Corrigan proposed that the synergistic effect between Fe and Ni could be related to either
1) a change in the conductivity of the electrocatalyst thin film, as a result of Fe doping, or by
2) the provision of more favourable sites for OER intermediates.#

Corrigan concluded that it is “unclear how the co-precipitated metal ions (Fe & Ni) exert their influence on the OER”

Trotochaud and Boettcher stated that “to date, no significant progress has been reported on this important question”.


Different Synthesis Routes of Ni(II) Oxide (NiO)

Thin Film (sputtering)

Nanoparticles (wet chemistry)

Commercial Samples

With and without Fe
Physical Characterisation of Ni(II) Oxide (NiO)

- Morphology – SEM, HRTEM
- Composition – EDX
- Structure – XRD
- Electronic structure & density of states – XPS
Electrochemical Characterisation of Ni(II) Oxide (NiO)

- Linear scanning voltammetry (LSV)
- Cyclic voltammetry (CV)
- Electrochemical impedance spectroscopy (EIS)
- Chrono-amperometry (CA)
- Chrono-potentiometry (CP)

- Characterisation
- Activity
- Durability

Perceived Activity
Pilot Scale Testing of Ni(II) Oxide (NiO)

Real Activity
Dissemination of Results / Progress

Annual Workshops & Meetings
- South Africa (NWU)
- Norway (NTNU)

Presentations at Conferences
- International Conference on Electrolysis (ICE)
- Annual meeting of the International Society for Electrochemistry

Publication of articles
Electrocatalysis, ACS Advanced Energy Materials, etc.

Progress Reports
Summary of planned activities

Collaboration will occur through:
• Student (MSc, PhD and Post Doc) and staff exchanges
• Workshops, conferences and meetings
• Joint publications and presentations

Next steps:
• Prof. Seland and Pollet to travel to NWU after SANOCEAN launch
• Prof. Kriek to travel to Norway in June 2019
  – Invited talk at a renowned international conference on electrolysis (ICE2019, Loen – Norway)
  – Visit to Trondheim after ICE2019
• Plan activities (exchanges, meetings and workshops) for upcoming reporting period
Thank you!