Development of proton conducting electrolyser cells

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High temperature electrolysers with novel proton ceramic tubular modules (2014-2017)

Fabrication of BZY-based segmented-in-series tubular electrolyser cells

Development of mixed proton-electron conducting anodes

Multi-tubes module development

H₂ production from steam and electricity

DME/Ethanol production from steam, CO₂ and electricity

Fabrication of BZY-based segmented-in-series tubular electrolyser cells

Development of mixed proton-electron conducting anodes

Multi-tubes module development
Solid State Reactive Sintering (SSRS)

Wet milling of precursor powders:
NiO + BaCO₃, Y₂O₃, ZrO₂, CeO₂

Drying of powders in oven

Pressing and sintering at T > 1400°C

BZCY based dense pellets with 1 wt. % NiO

- Limited number of processing steps
- Fine Homogeneous microstructure
- Fast sintering

- Cost effective
- Lower CO₂ emissions

- J. Tong, Ryan O'Hayre et al., J. Mater. Chem., 2010, 20
SSRS for enabling cells production in ELECTRA

BZY10: $\text{BaZr}_{0.90}\text{Y}_{0.10}\text{O}_{3-\delta}$
BZCY72: $\text{BaZr}_{0.70}\text{Ce}_{0.20}\text{Y}_{0.10}\text{O}_{3-\delta}$

Fuel electrode: NiO + $\text{BaCO}_3, \text{Y}_2\text{O}_3, \text{ZrO}_2$
Electrolyte: $\text{BaCO}_3, \text{Y}_2\text{O}_3, \text{ZrO}_2$

NiO+ BZY10 or NiO + BZCY72 (60/40 vol. %)

Notation: BZY10 // BZY10-NiO

Electrolyte

Electrode

and

Fuel electrode: NiO + $\text{BaSO}_4, \text{Y}_2\text{O}_3, \text{ZrO}_2$, with and without CeO$_2$
Electrolyte: $\text{BaSO}_4, \text{Y}_2\text{O}_3, \text{ZrO}_2$, with and without CeO$_2$
Solid state reactive sintering for BZY based cell production

- Pastes and suspensions
- Extrusion of fuel electrode
- Electrolyte deposition
- Co-sintering

SONATE 100 m² clean room

- Drying in air

- SONATE 100 m² clean room

- Dry milling of SSRS based precursors

- Dip-coating suspensions

- NiO based paste

- 40-ton extruder with automatic capping, cutting and air transport belt

- Automatic dip-coater Max 1m long tube

- 10-25 cm long tubes
Investigated parameters

- Fuel electrode extrusion
  - Paste formulation (solid loading, binder and water content)
  - Mixing procedure
  - Extrusion parameters
  - Drying and polishing

- Dip-coating of electrolyte
  - Suspension formulation (solid loading, binder content)
  - Milling procedure
  - Coating parameters

- Reduction of half-cells
  - Temperature
  - Atmosphere

- Co-sintering
  - Temperature, dwell time
  - Heating & cooling rates
  - Atmospheres
Drying and polishing

Tubes after extrusion and roll-drying in air for 24h

Close end from capping system

Dried tubes after polishing with wet clean room tissue

"Green" tubes after coating

15 cm
SSRS-based suspensions

- Water-based suspension
  *(cellulose based binder)*
  \( \text{BaSO}_4, \text{Y}_2\text{O}_3, \text{ZrO}_2, \text{CeO}_2 \)

- Organic-based suspension
  \( \text{BaCO}_3, \text{Y}_2\text{O}_3, \text{ZrO}_2, \text{CeO}_2 \)

Protocol:
Planetary milling of powders + binders + water or solvent @ 300 rpm – 2h

*Viscosity around 19 cP at 60 rpm using LV2 spindle*

*Viscosity 110-175 cP at 60 rpm with LV2 spindle*
BZY10 // BZY10-NiO using BaCO$_3$ based precursor mixture

1610°C - 6h: surface view of electrolyte

1610°C - 6h: surface view of uncoated electrode

BaNiY$_2$O$_5$

NiO

BaNiO$_2$
BZY10 // BZY10-NiO using BaCO$_3$ based precursor mixture

1550°C - 24h

Ba$_2$NiY$_2$O$_5$

BaNiO$_2$
BZY10 // BZY10-NiO using \( \text{BaCO}_3 \) based precursor mixture

Wet 4\%H\(_2\)/Ar @ 900°C

Cracks in electrolyte

\( \text{Y}_2\text{O}_3 \)

\( \text{BaNiY}_2\text{O}_5 \)

\( \text{Ni} \)

\( \text{BaNiY}_2\text{O}_5 \)
SSRS BZY pellet with 2wt% NiO

![Dilatometry in air HT XRD](image)

![Graph showing thermal expansion vs. temperature](image)

$\text{BaNi}_2\text{Y}_2\text{O}_5$

Temperature (°C) vs. Thermal expansion (%)

SSRS BZY pellet with 2wt% NiO

\[
\text{BaNiY}_2\text{O}_5
\]

4 microns

1 microns

θ
Investigated half-cells with $\text{BaSO}_4$ precursor
BZCY72 // BZCY72-NiO

Dense electrolyte @
1550°C – 24h
1610°C – 6h

BZY10 // BZY10-NiO

Dense electrolyte @
1550°C – 24h
1610°C – 6h

BZY10 // BZCY72-NiO

Dense electrolyte @
1550°C – 24h
1610°C – 6h
BZCY72 // BZCY72-NiO

1550°C – 24h

Grain size:
Large: 5 microns
Small: 2 microns

Grain growth

1610°C – 6h

Grain size:
5-10 microns
Reduction of half-cells

- Wet Harmix at 900°C

![Image showing a microstructure with a scale of 40 microns]

**Hg-porosimetry**

- Between 27-32 vol% porosity (with 60 vol% Ni)
BZY10 // BZY10-NiO

1610°C - 6h
"BZY10" // BZCY72-NiO

2% Ce in BZY

100 microns

10 microns
Characterization

Phases evolution
- HT-XRD up to 1200°C
- TGA / DSC up to 1400°C
- • BaSO₄
- • BaSO₄, Y₂O₃, ZrO₂, CeO₂ or without CeO₂
- • NiO - BaSO₄, Y₂O₃, ZrO₂, CeO₂ or without CeO₂

Microstructural evolution
- HT-ESEM up to 1400°C
- Ex-situ SEM-EDS analyses
- • Green half-cells
- • Green coated half-cells
- • Half-cells annealed from 1550°C – 1670°C

Sintering behaviour
- Dilatometry (push rod) up to 1500°C
- Fast sintering up to 1600°C
- • BaSO₄, Y₂O₃, ZrO₂, CeO₂ or without CeO₂
- • NiO - BaSO₄, Y₂O₃, ZrO₂, CeO₂ or without CeO₂
- • Green half-cells
BaSO₄

Ortho to cubic

Shift in relative peak intensity

TGA/DSC in air & HT-XRD

XRD: BaSO₄ Pbnm

Optical dilatometry
NiO - BaSO$_4$, Y$_2$O$_3$, ZrO$_2$, CeO$_2$

SSRS mixture BZY10-NiO
SSRS mixture BZCY72-NiO
BaSO$_4$ powder
Heating to 1600°C @ 2°C/min - 10 min dwell

NiO ensures mechanical strength

BZY10 // BZY10-NiO

BZCY72 // BZCY72-NiO

BZCY72+NiO ensure mechanical strength
Summary

• Sintering of BZY10 electrolyte not yet achieved
  • Further experiments in progress to understand limiting factors

• Successful fabrication of tubular half-cells with BCZY based electrolytes (20%Ce; 2%Ce)
  • Samples are given for air electrode development

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Thank you