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Proton Ceramic Steam Electrolysers

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Electra

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

- Theoretical considerations on electrolysis operation
- Development and performance of tubular Proton Ceramic Electrolysers (PCEs)

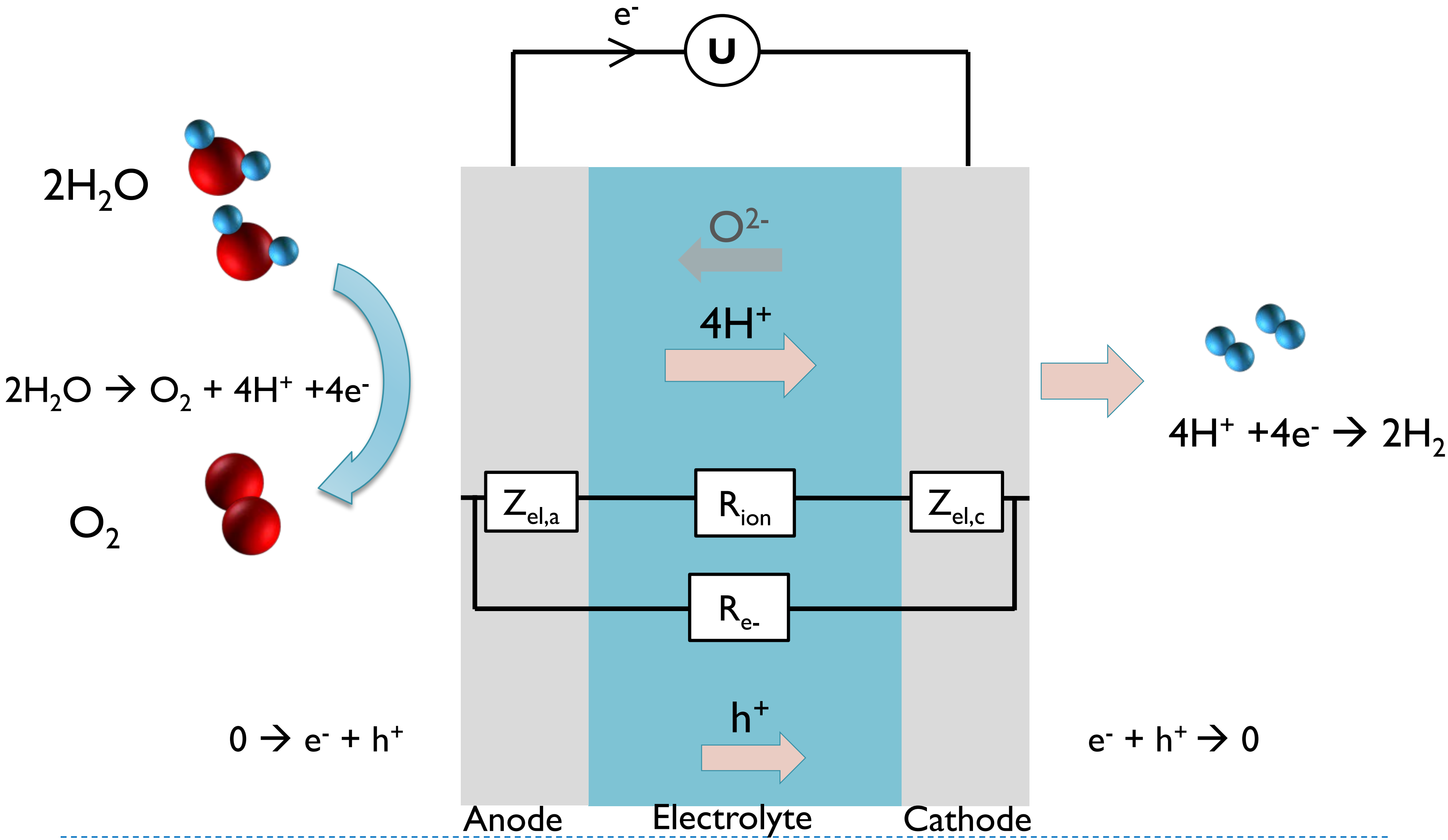
Literature data for Proton Ceramic Electrolysers (PCEs)

Key question:
What is the origin of the low faradaic efficiencies observed in many PCEs?

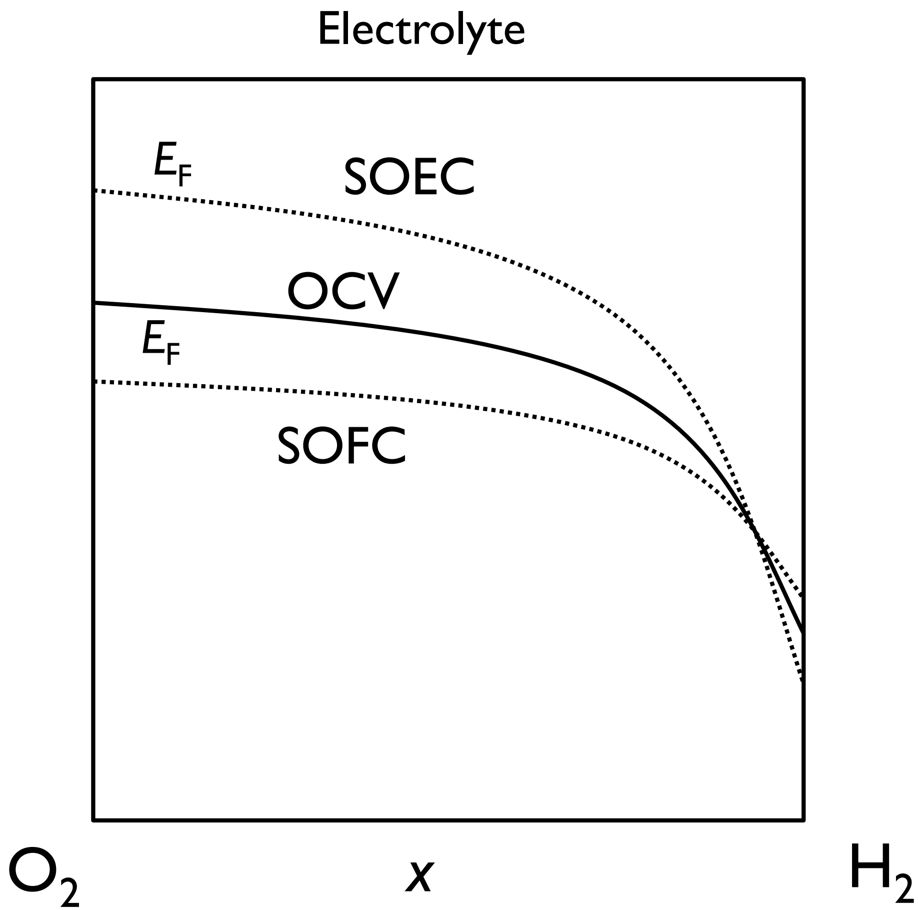
Electrolyte	Anode	Temperature	i (mA cm^2)	ASR (Ωcm^2)	η (%)	Ref
SSY541	SSC	600	100	4	~80	Matsumoto, 2012
BCZY53-Zn	BSCF	800	55	20	50	Li, 2013
BZCY72	LSCF	700	100	6	50	Babiniec, 2015
BCZY53-Zn	LSCM-BCZYZ	700	2000	6-8	22	Gan, 2012
BCZY62	BSCF	600	1050	0.5	99 (?)	Yoo, 2013
BCZY53	SSC-BCZY	700	400	1	-	He, 2010

Degradation and decomposition in H_2O

Operating Principles of Proton Ceramic Electrolysers (PCEs)

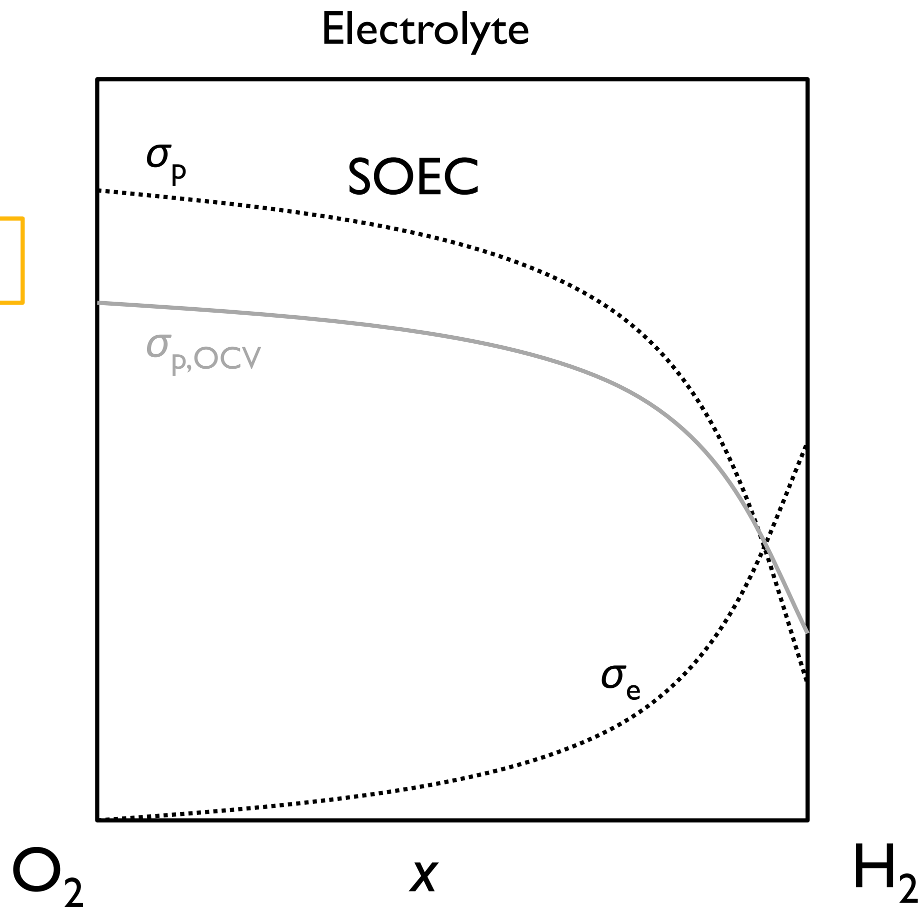


Potentials through a solid oxide electrolyser

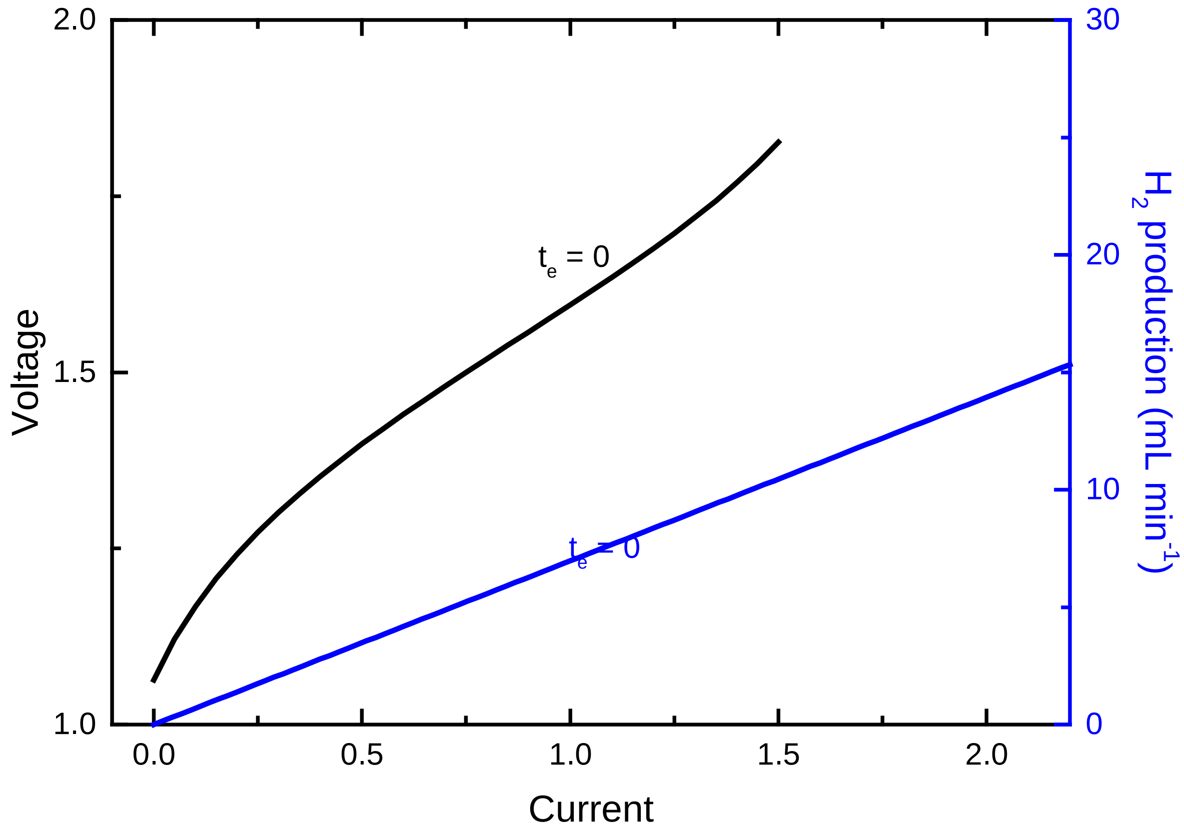


Electronic conductivity distribution during PCE operation

$\sigma_p \propto pO_2^{1/4} \propto \exp(E_F/4)$



The effect of partial electronic conductivity on faradaic efficiency



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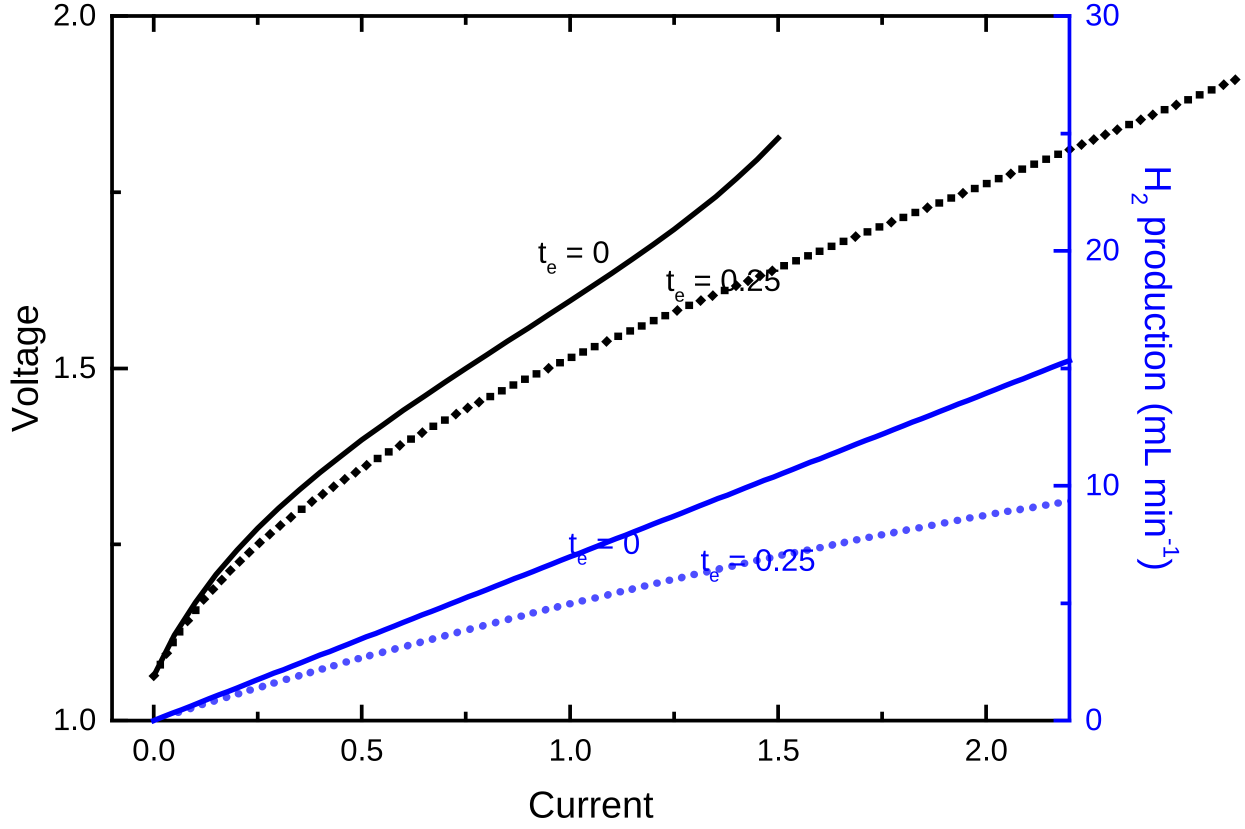
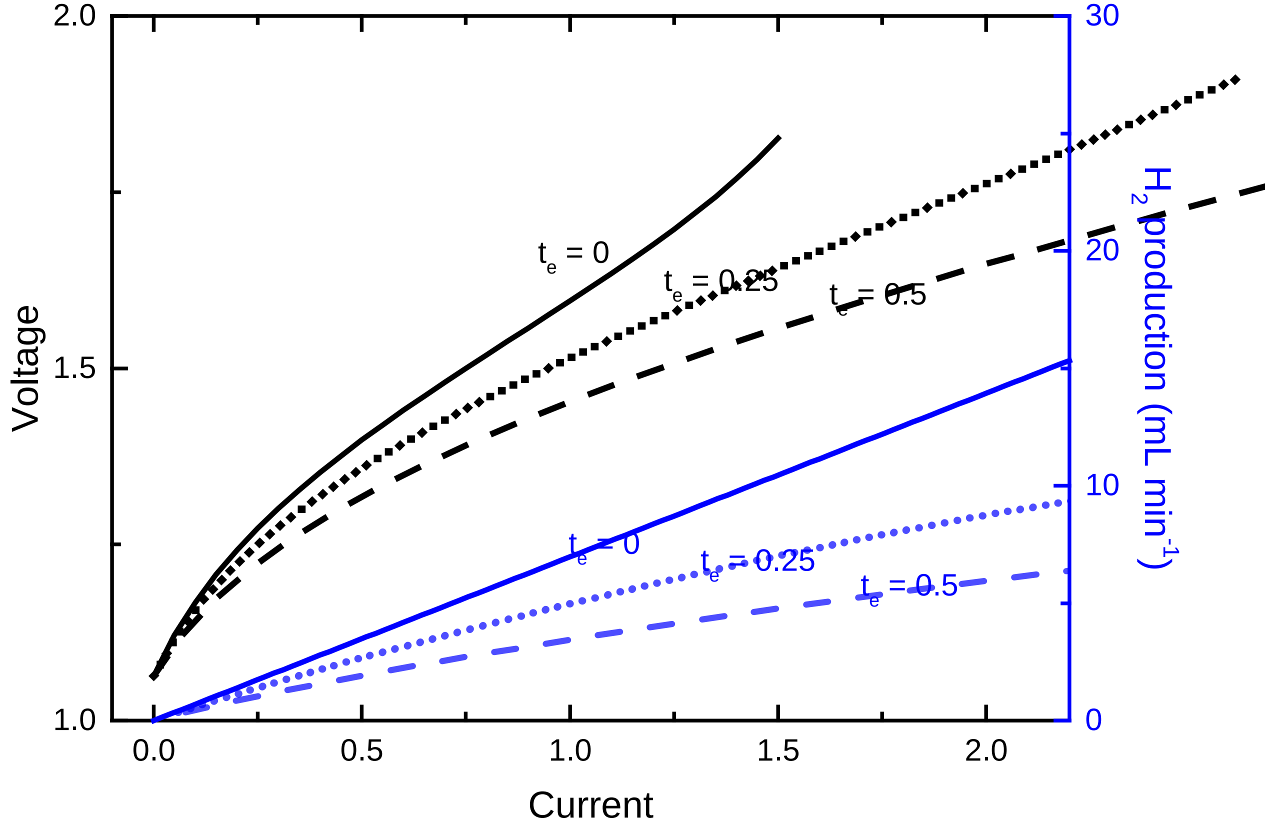


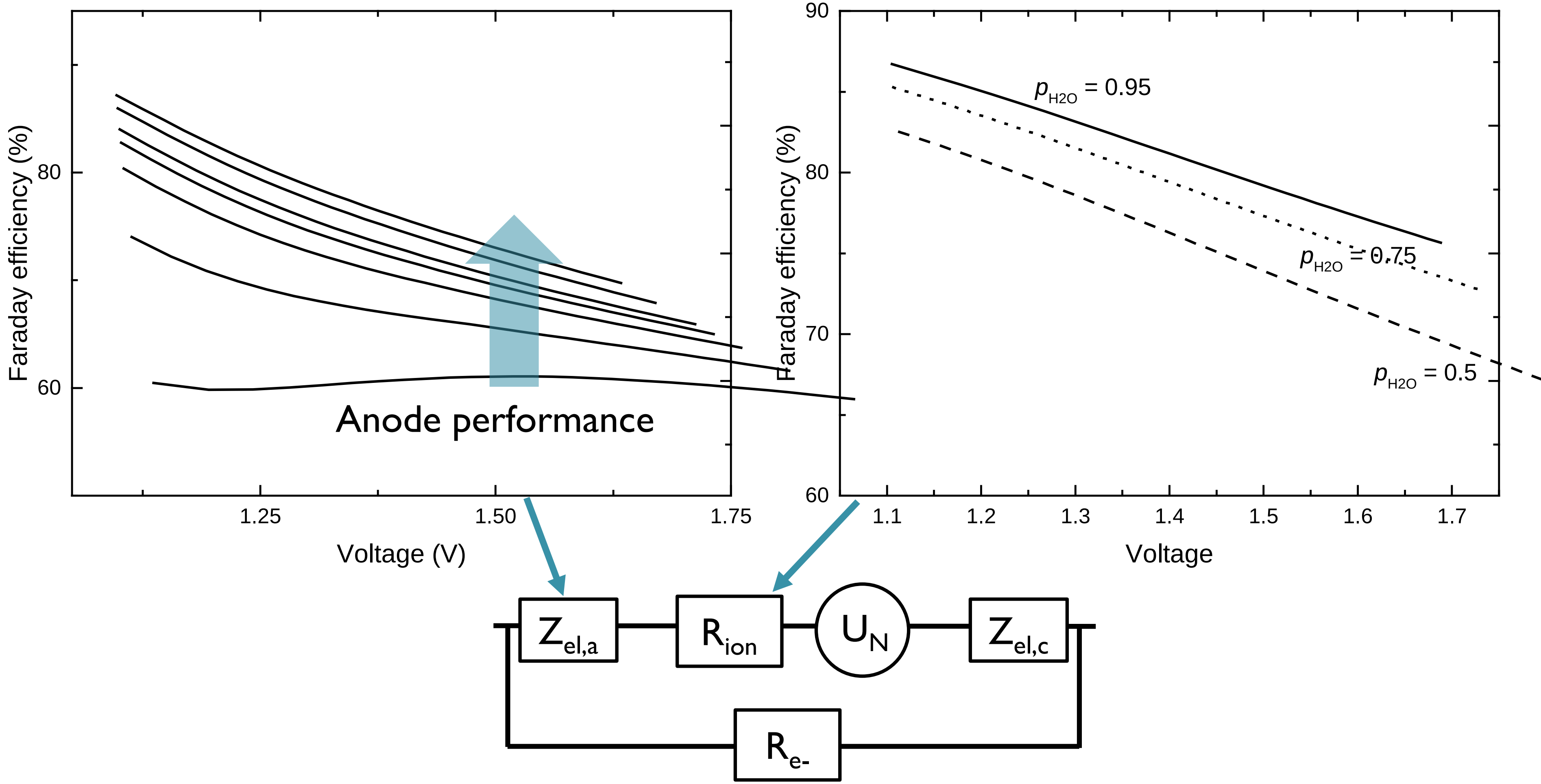
The effect of partial electronic conductivity on faradaic efficiency



Electrode performance and steam content significantly influence faradaic efficiency

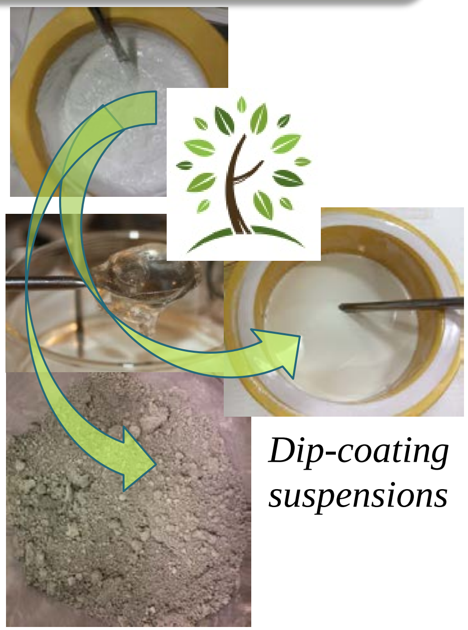
Anode dependence for with fixed t_H = 0.8

Steam content dependence with fixed t_H = 0.8



Tubular half-cell production

Wet milling of precursors

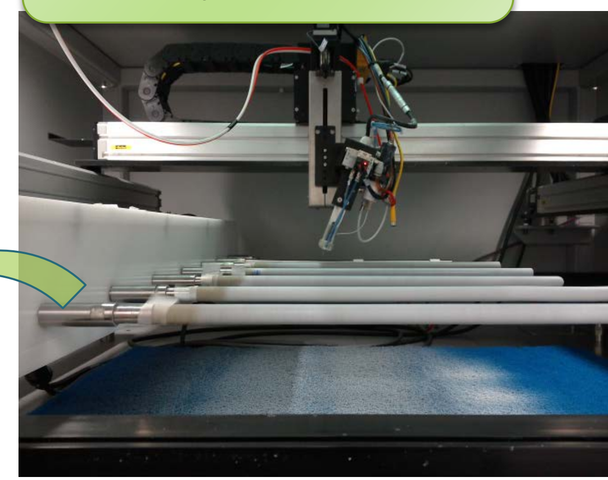


Dip-coating suspensions

NiO based paste

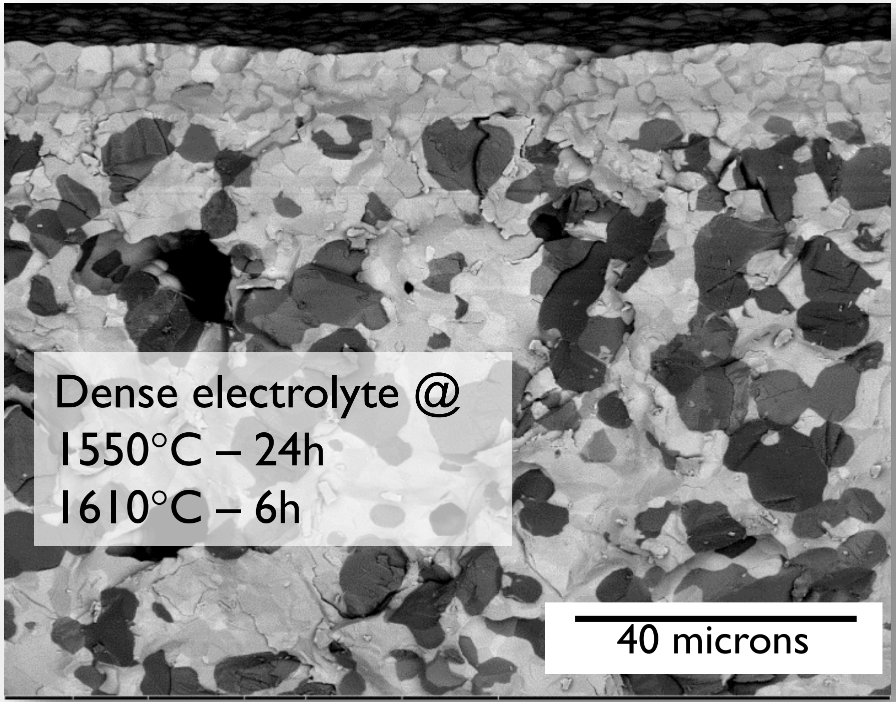
Extrusion of BZCY72-NiO support

Spray-coating BZCY72 electrolyte



Solid State Reactive Sintering

Dense tubular half-cells achieved



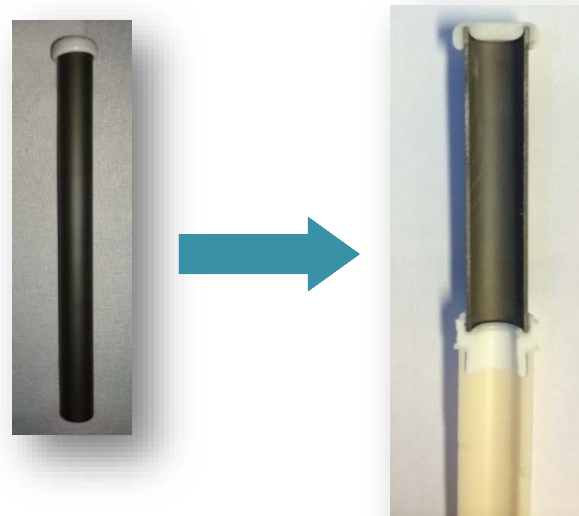
Steam electrode processing on reduced tubes

1. Cap and seal segment using glass ceramic from CoorsTek

2. Deposit $Ba_{0.7}Gd_{0.8}La_{0.5}Co_2O_{6-\delta}$ as steam electrode by paint brush

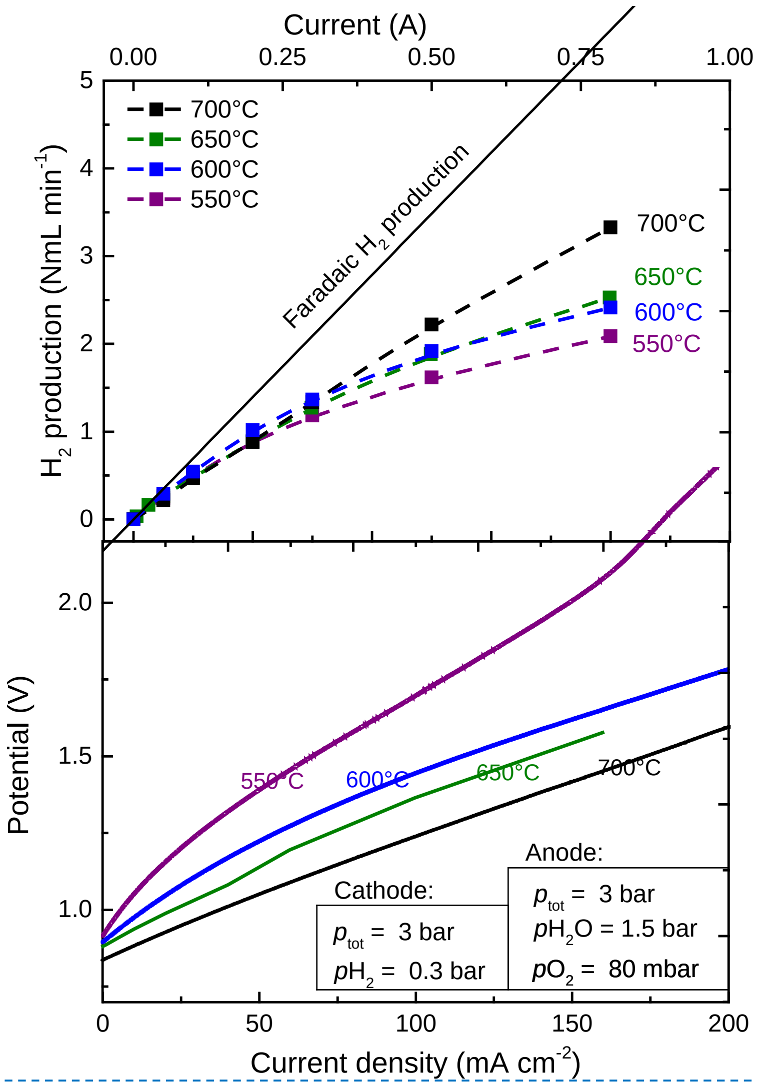
3. Firing in dual atmosphere:
   - 1000°C
   - 2% O_2 outside, 5% H_2 inside
   - E_{cell} = 1.4 V during firing

4. Gold paste applied as current collector

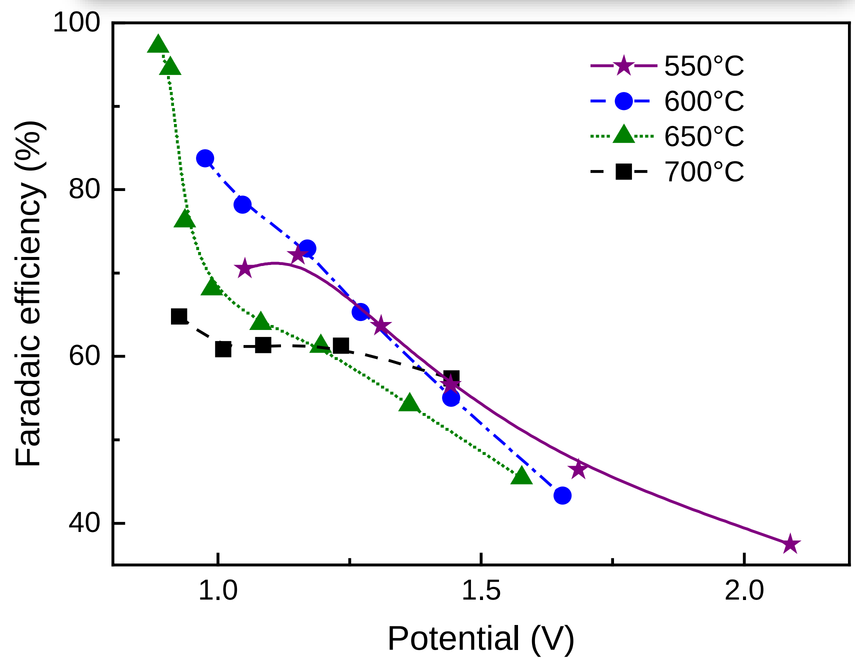


Cell 1

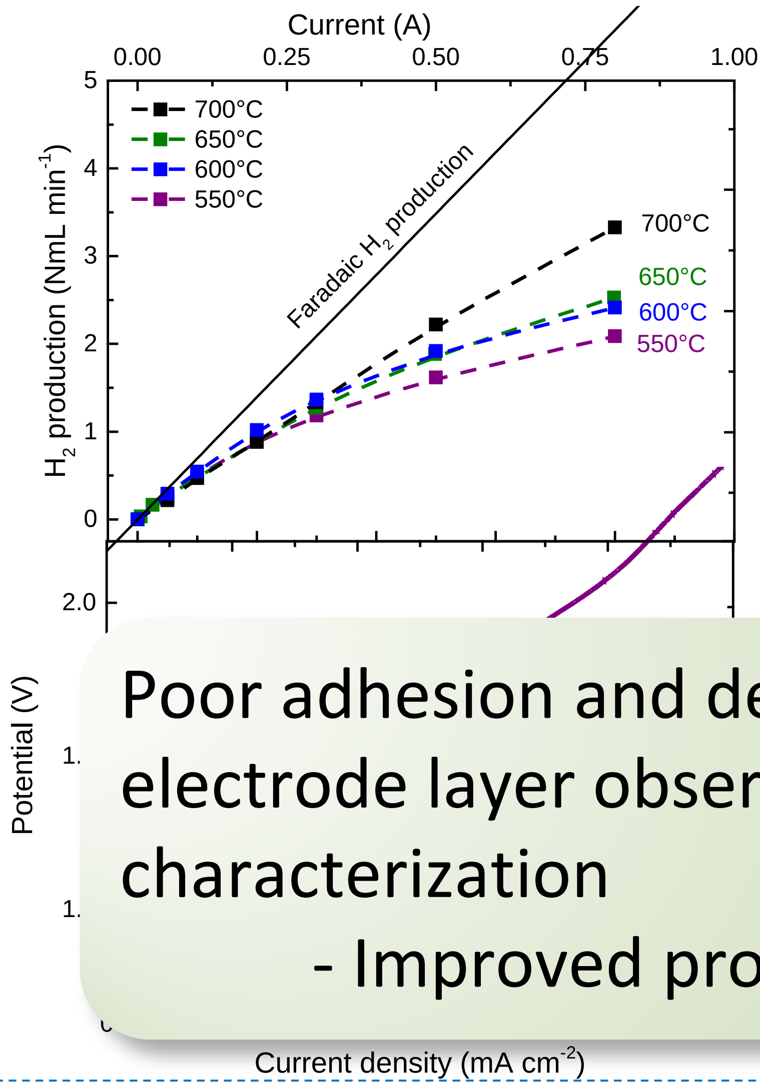
Electrolysis with single phase BGLC electrode



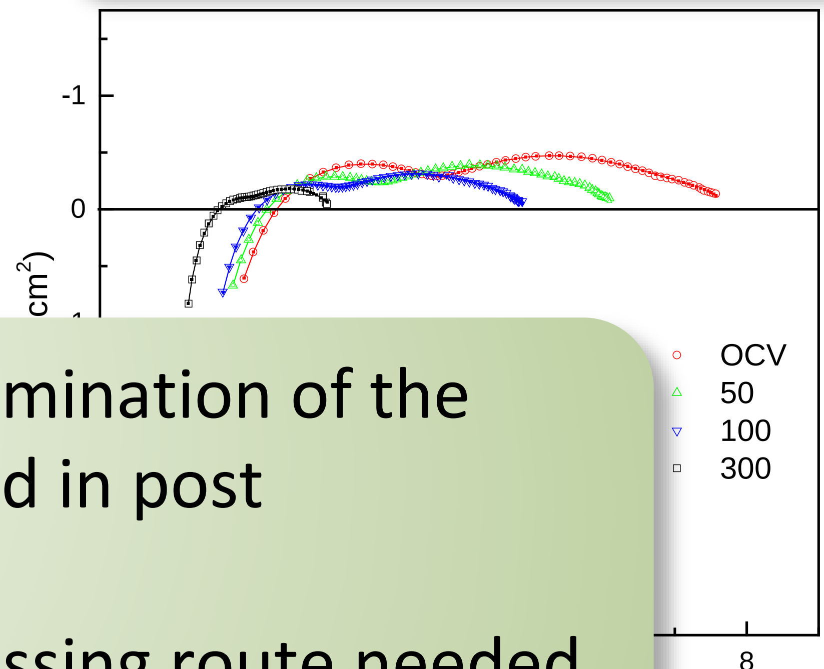
Faradaic efficiencies vs cell potential



Electrolysis with single phase BGLC electrode



Impedance at 600°C for increasing galvanostatic bias



Poor adhesion and delamination of the electrode layer observed in post characterization

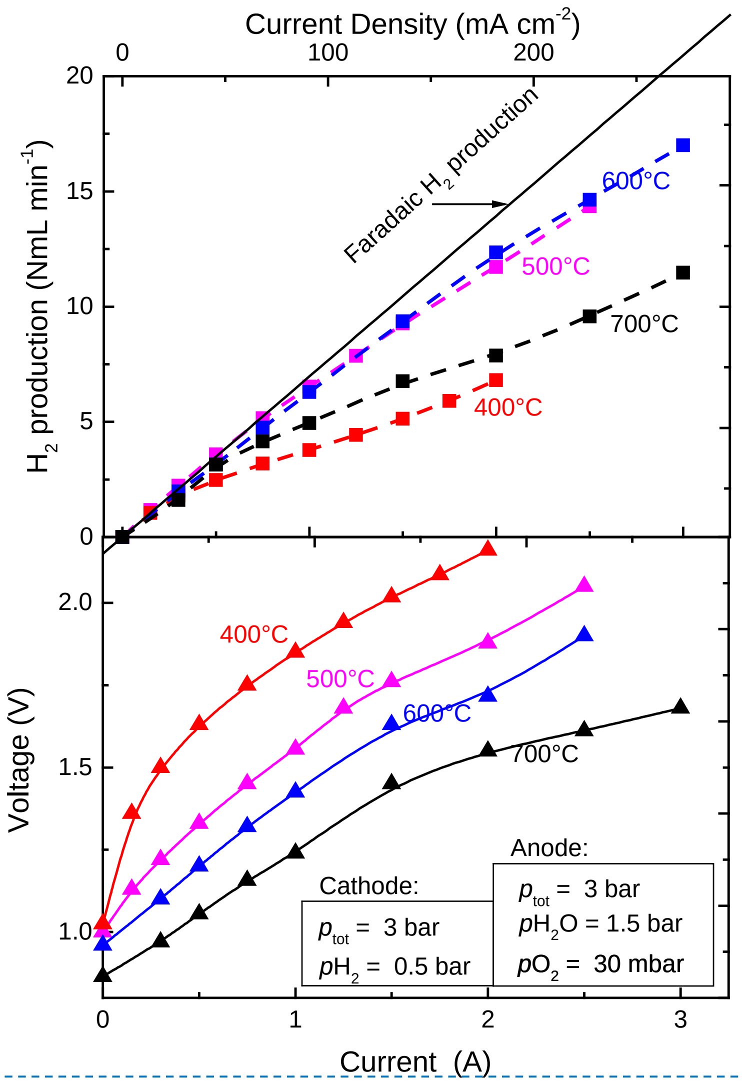
- Improved processing route needed

Steam electrode processing on unreduced tubes

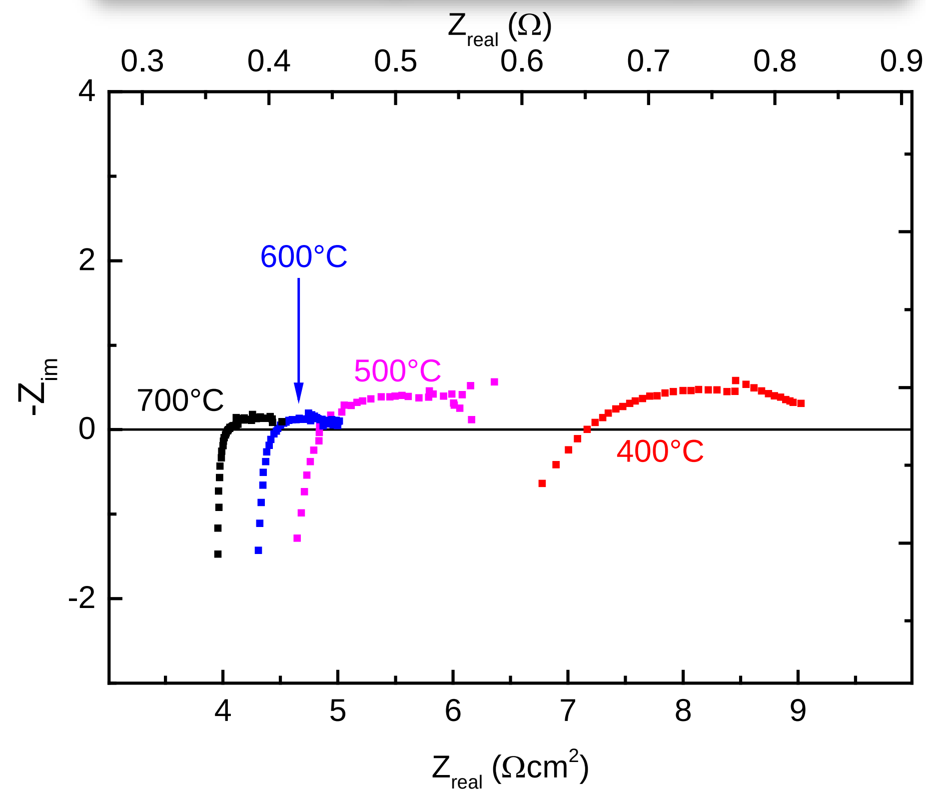
1. BZCY72- $Ba_{0.5}Gd_{0.8}La_{0.7}Co_2O_{6-\delta}$ applied as steam electrode
   - Fired in air at 1200°C for 5h
   - Infiltrated with nanocrystalline $Ba_{0.5}Gd_{0.8}La_{0.7}Co_2O_{6-\delta}$
   - Thin Pt layer current collection
2. Capped and sealed at 1000°C
   - Semi-dual atmosphere to keep BGLC layer intact
3. NiO reduction at 800°C in 10% H_2 for 24h
   - Kept in electrolytic bias during reduction to avoid re-oxidation

Cell 2

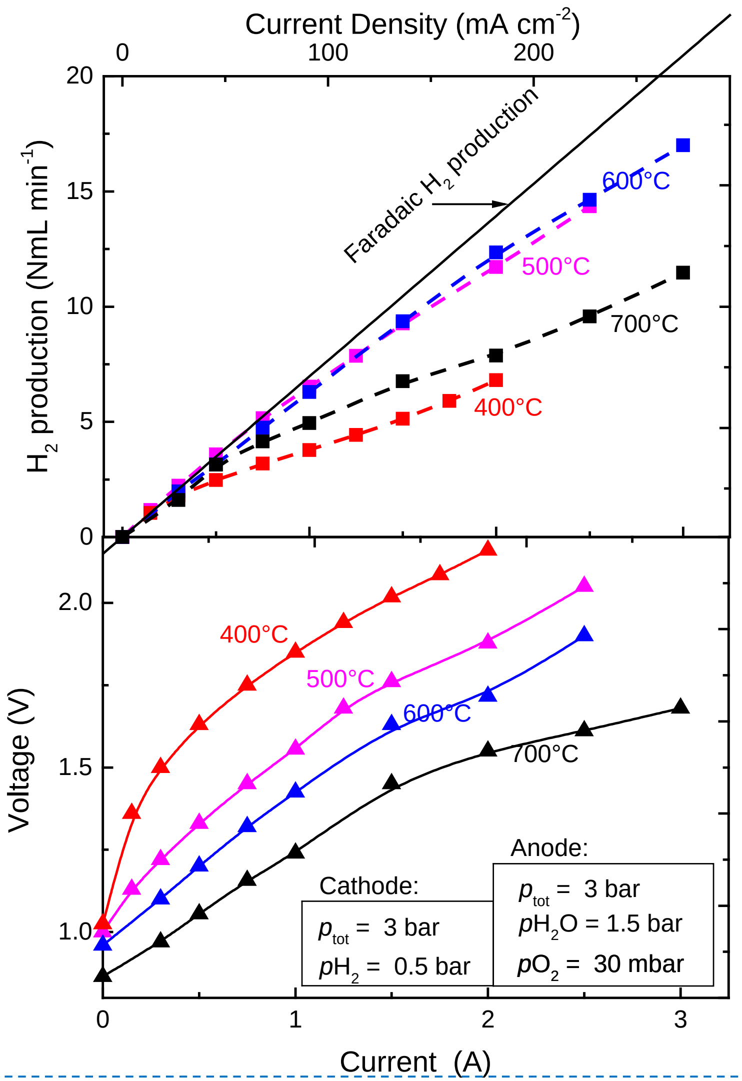
Electrolysis with composite BZCY-BGLC electrode



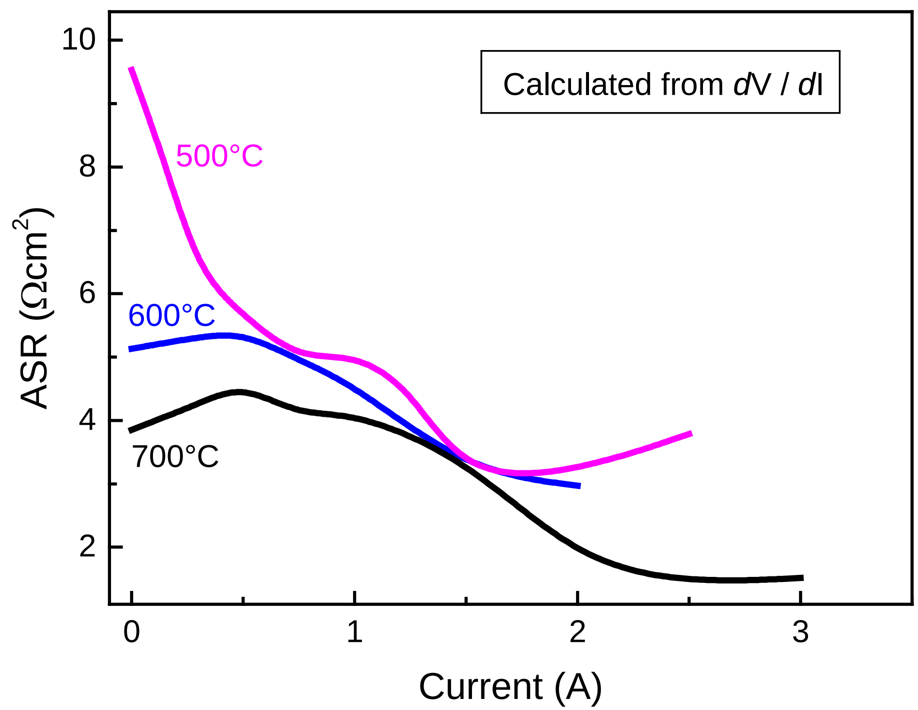
EIS at 300mA galvanostatic operation



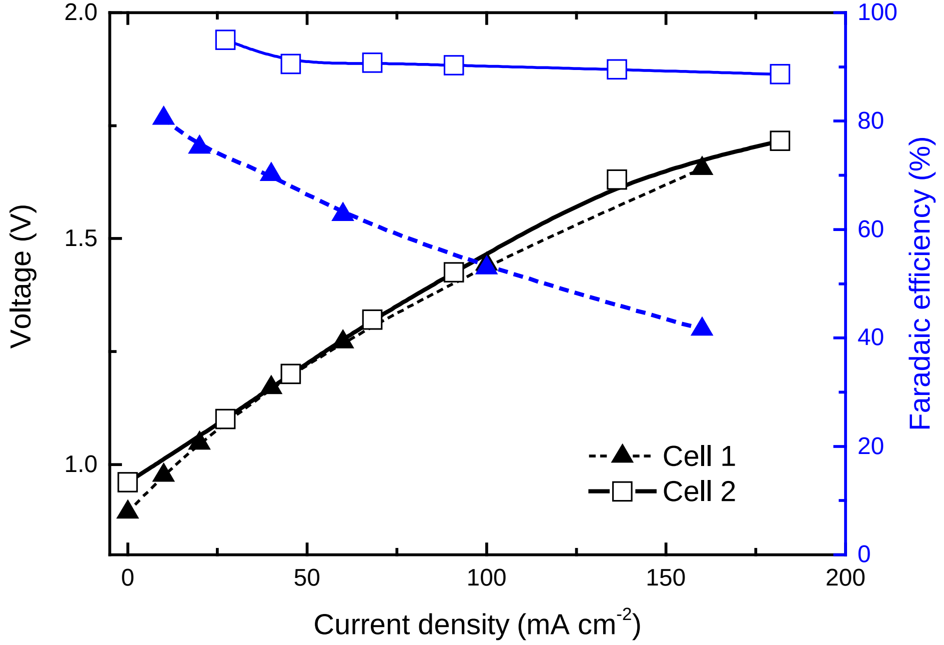
Electrolysis with composite BZCY-BGLC electrode

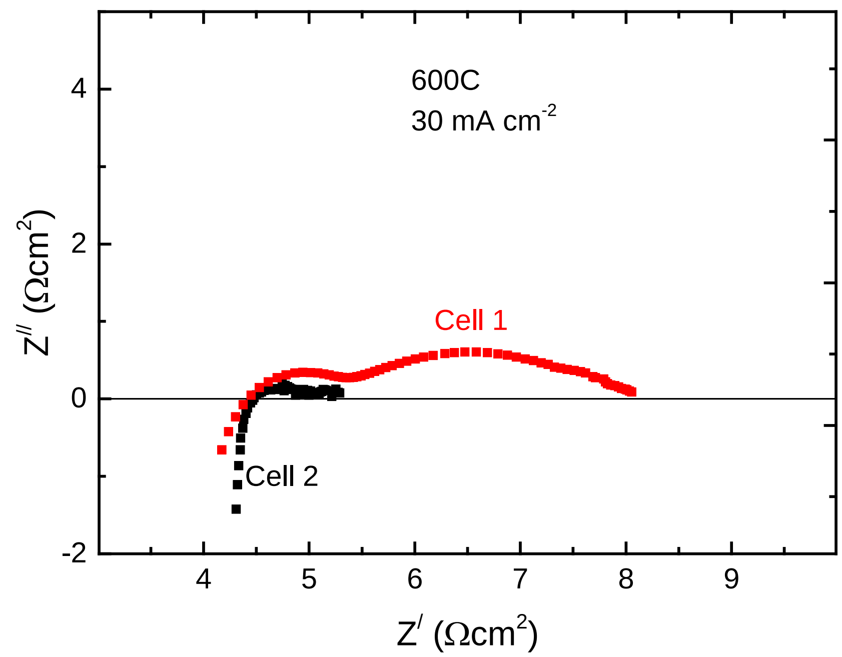


Calculated ASR from IV curves



Improved faradaic efficiency primarily due to enhanced electrode kinetics





Conclusions

- Proton Ceramic Electrolysers may suffer from electronic leakage during operation due to relatively high p-type conductivity in oxidizing conditions
  - Operation at **high overpotentials** will induce **higher electronic conductivity** within the electrolyte material
  - Improved **electrode performance** and **higher steam pressures** may reduce electronic leakage

- Tubular PCEs were made based on BZCY-NiO tubular supports, spray coated BZCY72 electrolytes and BGLC steam electrodes
  - **Enhanced faradaic efficiencies** observed with improved anode performance
  - Current densities of **220 mA cm^{-2} at 600°C** observed with > **80% faradaic efficiency**
  - Contact resistance may still contribute significantly to the ohmic resistance of the electrolyser

Acknowledgements

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