Fuel processing of H_2/CO_2 mixtures from biohydrogen production processes in solid oxide cell devices

Christian J. Laycock, Kleitos Panagi, James R. Reed and Alan J. Guwy

Sustainable Environment Research Centre, University of South Wales, UK

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Presentation Contents

- Electrochemical characterisation of a commercially available button SOFC running on H_2/CO_2 mixtures simulating gases from biohydrogen production processes
- Characterisation of fuel processing using quadrupole mass spectrometry
- Characterisation of fuel variability on cell performance and fuel processing
- Comparison of cell performance in fuel cell mode and electrolysis mode

Biohydrogen

- Biohydrogen production processes include dark fermentation, photofermentation, biophotolysis and bioelectrochemical techniques

✓ Biohydrogen does not contain methane and SOFC efficiencies are better with hydrogen

✓ Better SOFC resistance to carbon deposition and sulfur poisoning

✓ Versatility: electrochemical reduction of CO_2 potentially yields synthesis gas (H_2 + CO)

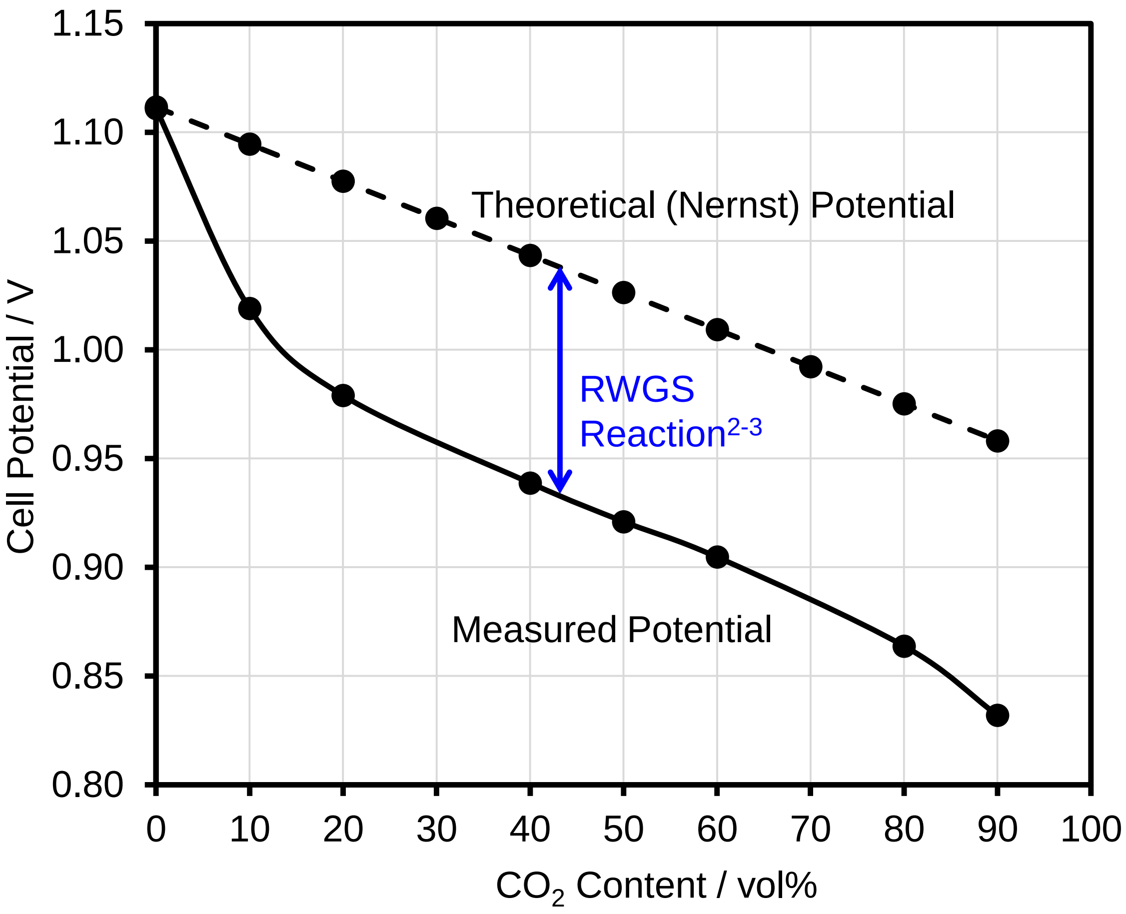
Composition of biohydrogen[1].

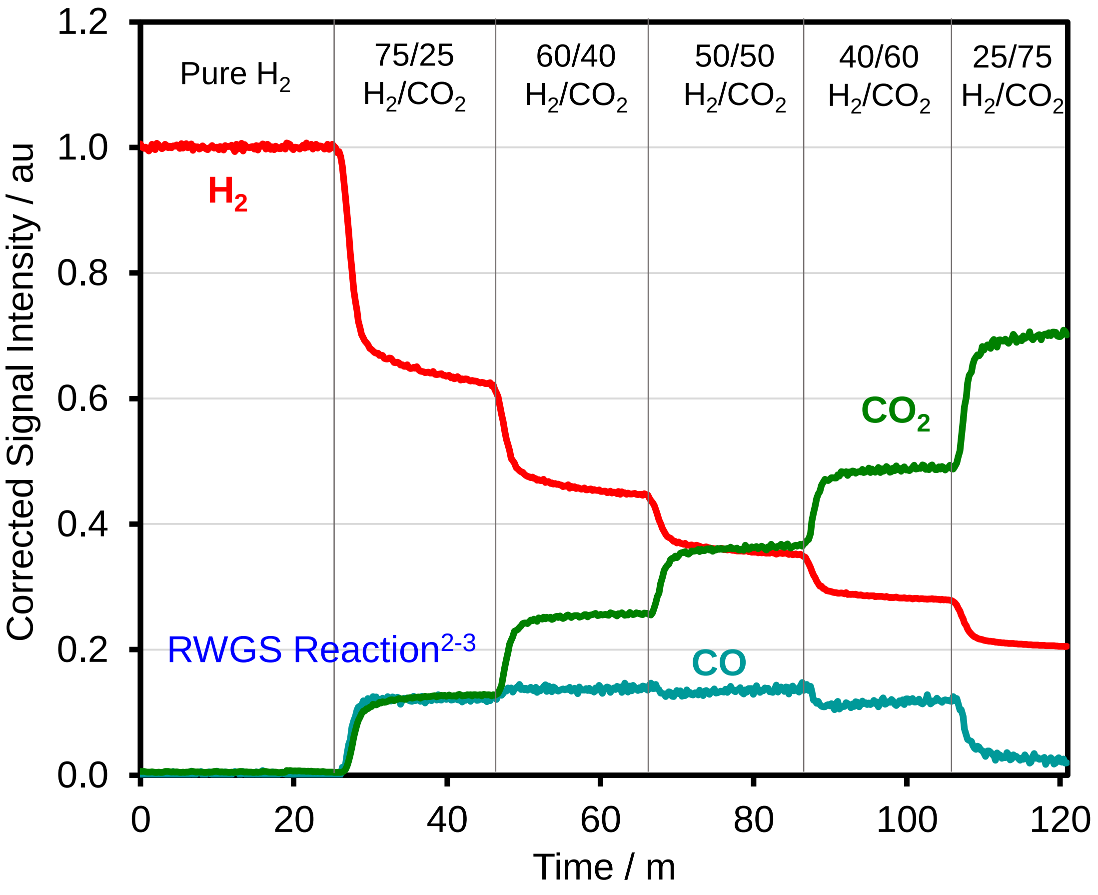
Component	Content
Hydrogen	40-50 vol%
Carbon dioxide	50-55 vol%
Nitrogen	3-8 vol%
Oxygen	1-4 vol%
Carbon monoxide	< 0.001 vol%
Methane	< 0.01 vol%
Sulfur-containing compounds	< 200 ppm
Other impurities	< 2 vol%

[1]Leone *et al*. J.Power Sources 195 (2010) 239-248.

OCP Measurements

ESC (FCM, 213205)
Temperature: 800 °C





RWGS Reaction: $H_2 + CO_2 \rightleftharpoons H_2O + CO$ $\Delta H = +75 \text{ kJ mol}^{-1}$

[2]Wolf *et al*. Chem. Eng. Technol. 39 (2016) 1040-1048.
[3]Lu *et al*. Mater. Res. Bull. 53 (2014) 70-78.

Fuel Cell Mode – 50/50 vol% H_2/CO_2

Hydrogen Conversion:

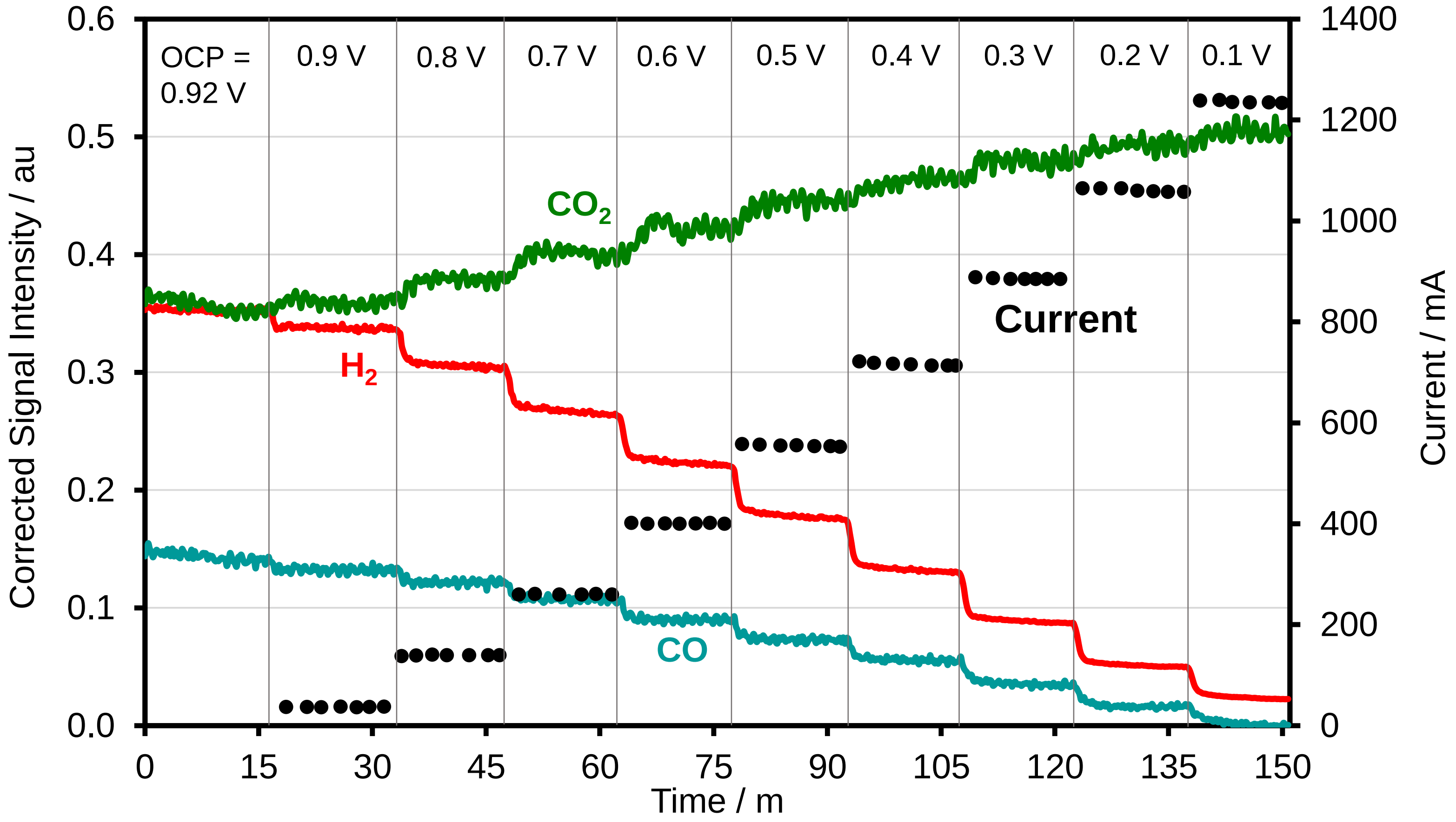
$H_2 + O^{2-} \rightleftharpoons H_2O + 2e^-$

CO Conversion:

$CO + O^{2-} \rightleftharpoons CO_2 + 2e^-$

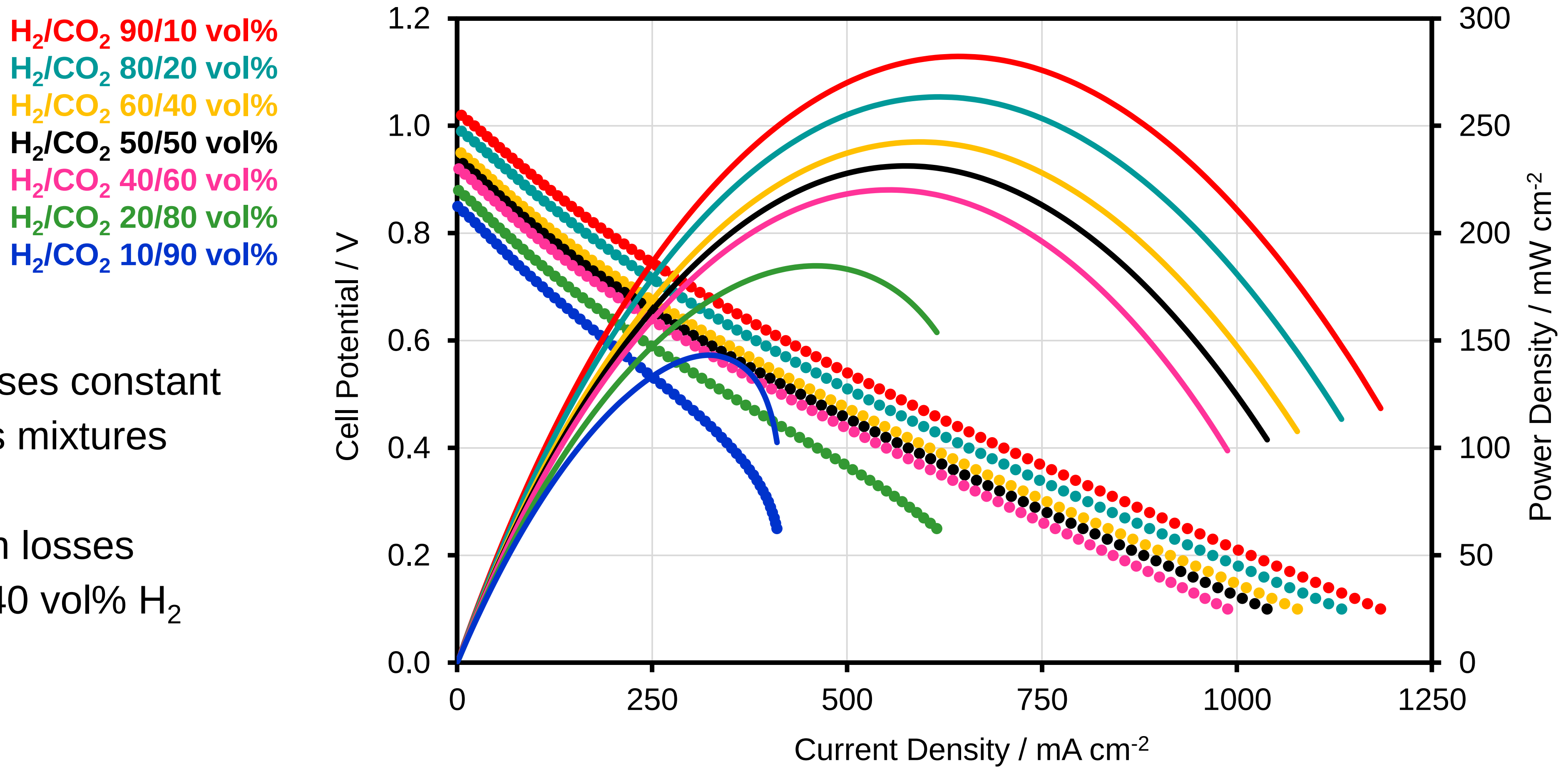
(very slow when

$H_2 >> CO$)[4-5]



[4]Holtappels *et al*. J. Appl. Electrochem. 29 (1999) 561-568.
[5]Weber *et al*. Solid State Ion. 152-153 (2002) 543-550.

I-V Curve Measurements

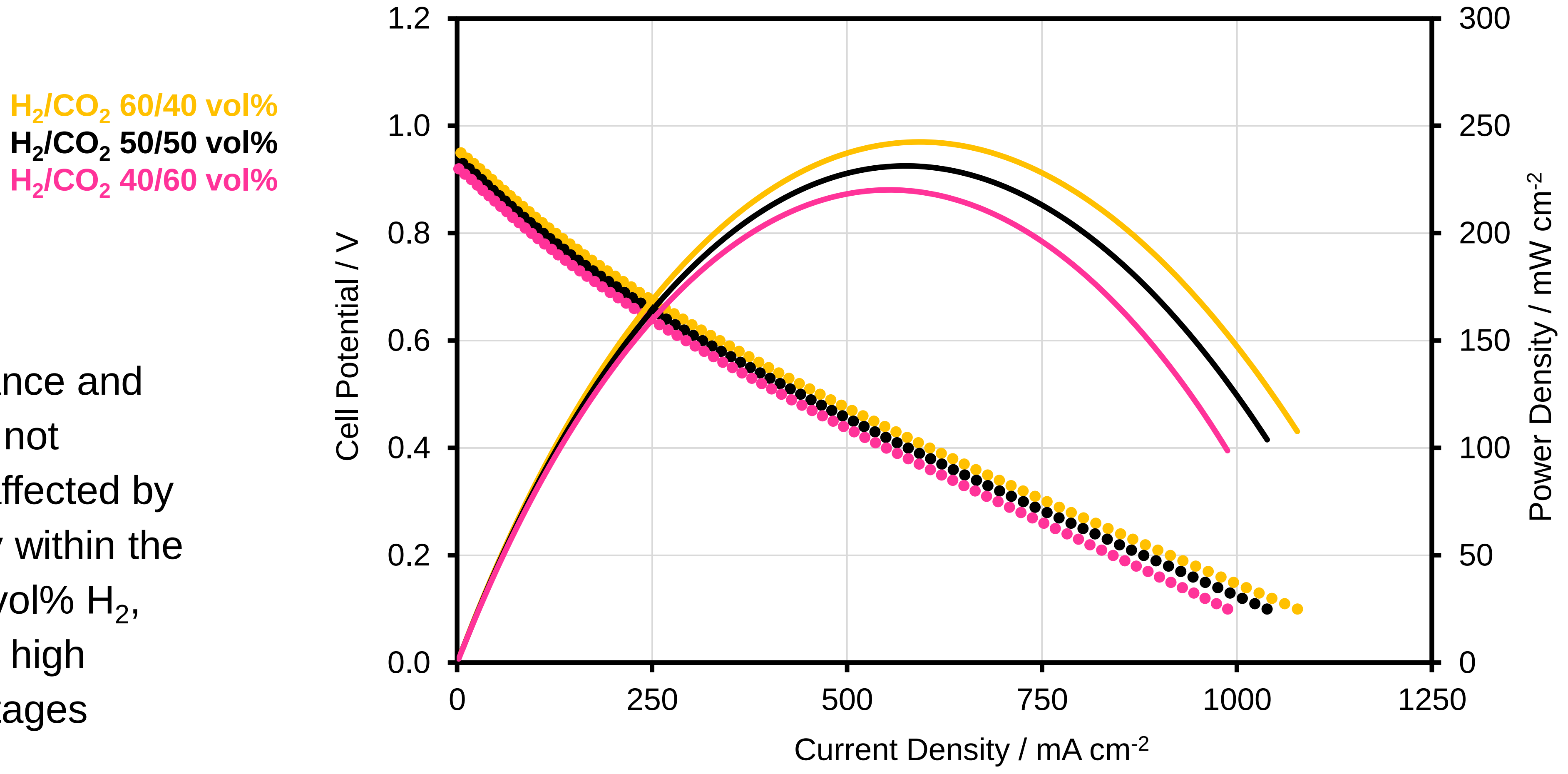


Activation losses constant across all gas mixtures

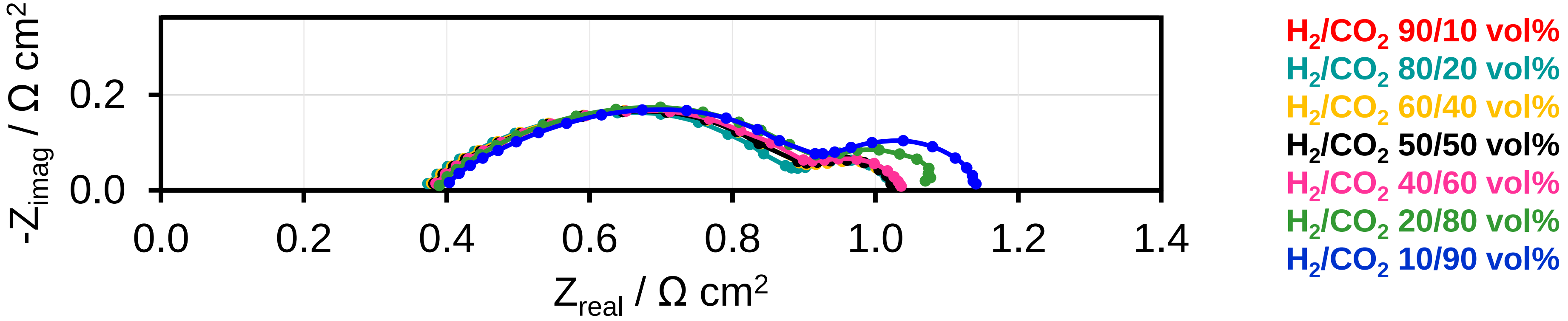
Concentration losses present at < 40 vol% H_2

I-V Curve Measurements

Cell performance and power output not significantly affected by fuel variability within the range 40-60 vol% H_2, particularly at high operating voltages



Fuel Cell Mode Impedance



Low frequency arc width increases when H_2 < 40 vol%: increased diffusion losses[6] over this range

High frequency arc width constant: no electrochemical[6] CO conversion

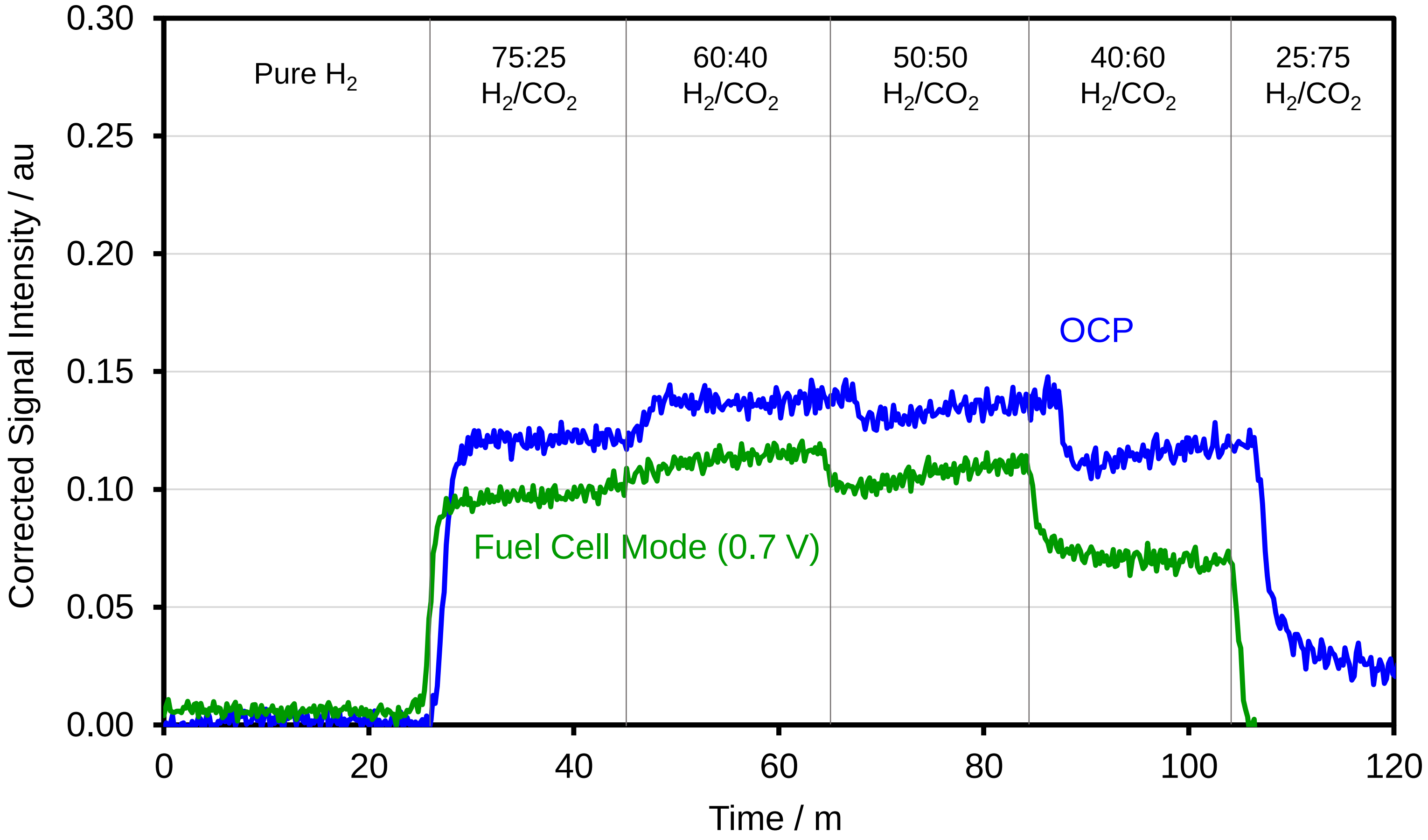
[6]Zhan *et al*. Energy Fuels 23 (2009) 3089-3096.

H_2/CO_2 vol%	High Frequency Arc Width / Ω cm^2	Low Frequency Arc Width / Ω cm^2
80:20	0.5179	0.1316
60:40	0.5248	0.1245
50:50	0.5217	0.1214
40:60	0.5269	0.1240
20:80	0.5276	0.1530
10:90	0.5121	0.2255

CO Production

Equilibrium of RWGS reaction (and therefore CO production) varies as the fuel composition is changed

Therefore, if CO conversion were electrochemical, the activation overpotentials would also change with fuel composition



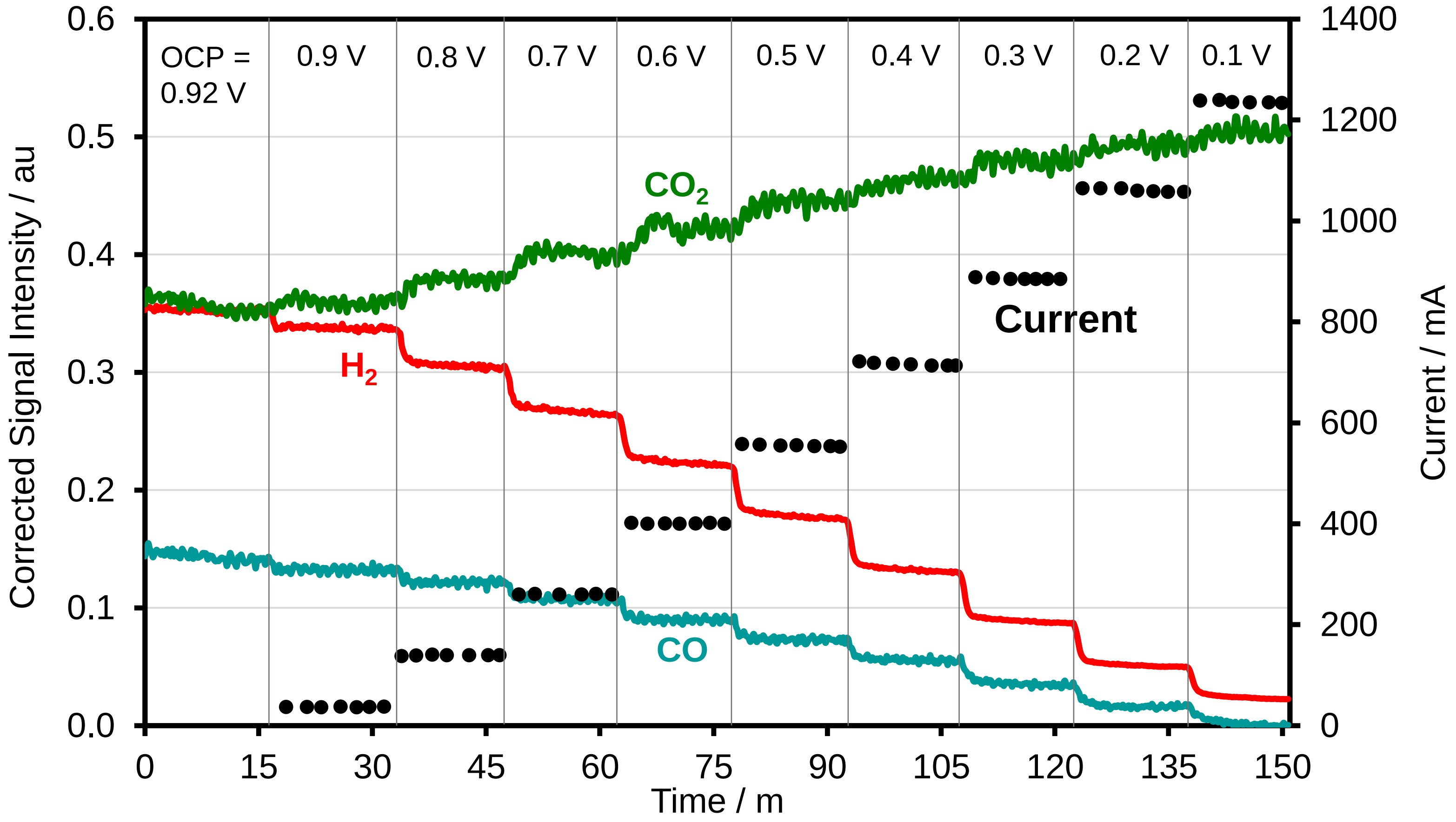
CO Conversion in Fuel Cell Mode

Hydrogen Conversion:

$H_2 + O^{2-} \rightleftharpoons H_2O + 2e^-$

Electrochemical H_2 oxidation shifts RWGS reaction:

$H_2 + CO_2 \rightleftharpoons H_2O + CO$



Electrolysis Mode – 50/50 vol% H_2/CO_2

Reverse Water-Gas Shift:

$H_2 + CO_2 \rightleftharpoons H_2O + CO$

Hydrogen Production:

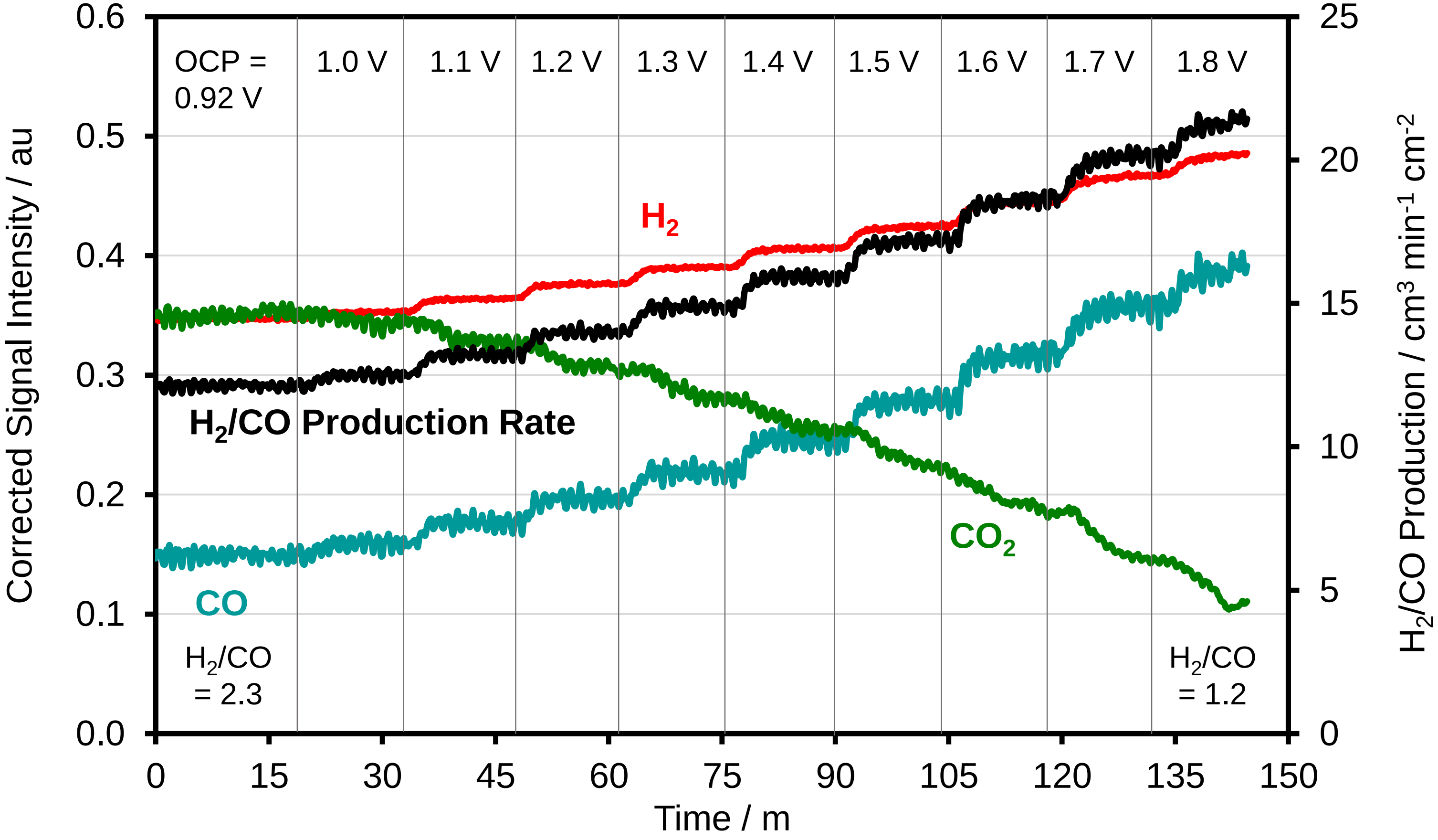
$H_2O + 2e^- \rightleftharpoons H_2 + O^{2-}$

CO Production[7-8]:

$CO_2 + 2e^- \rightleftharpoons CO + O^{2-}$

or

$H_2 + CO_2 \rightleftharpoons H_2O + CO$

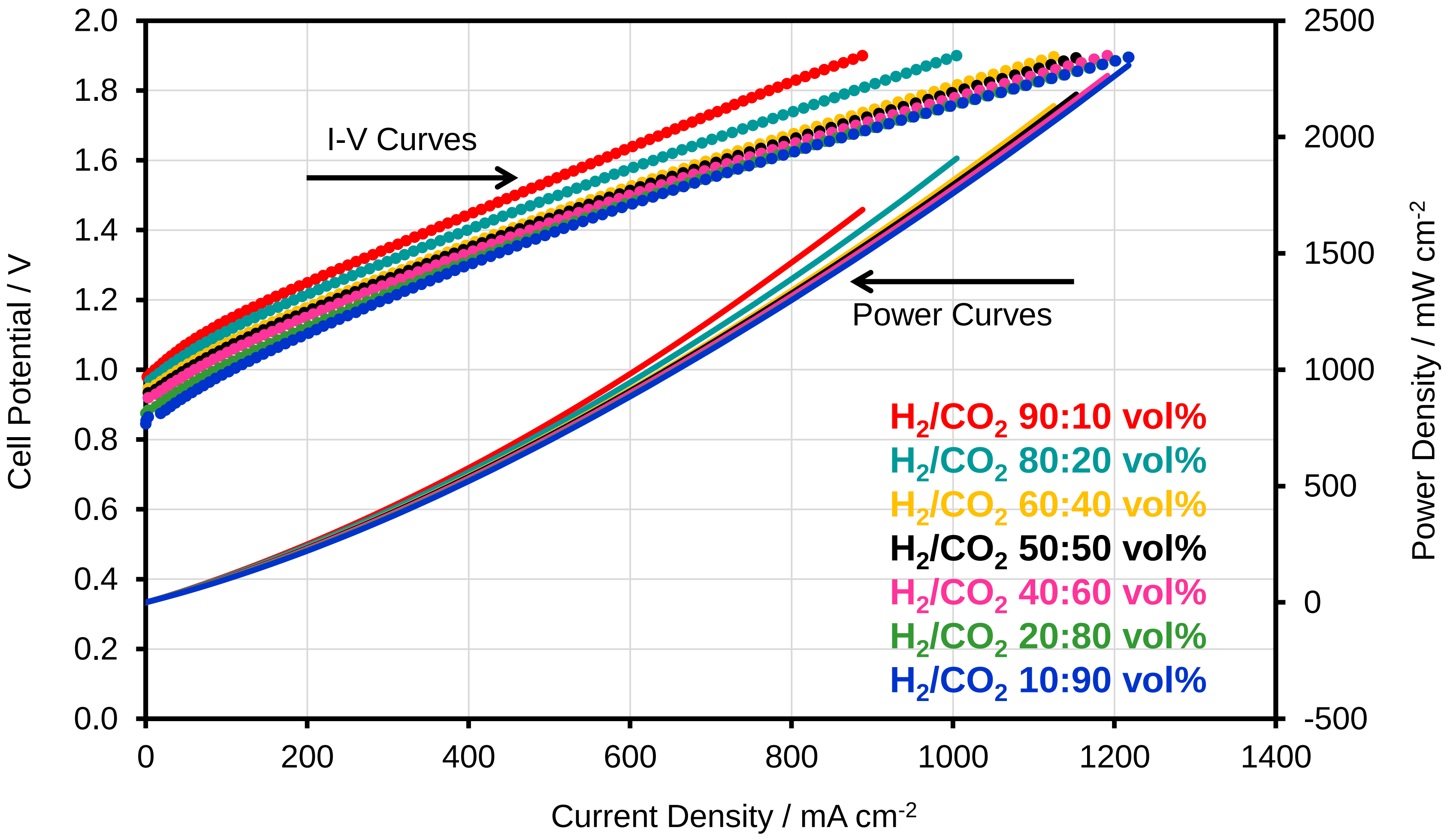


[7]Matsuzaki *et al*. J. Electrochem. Soc. 147(5) (2000) 1630-1635.
[8]Jiang *et al* J. Electrochem. Soc. 150(7) (2003) A942-A951.

I-V Curve Measurements

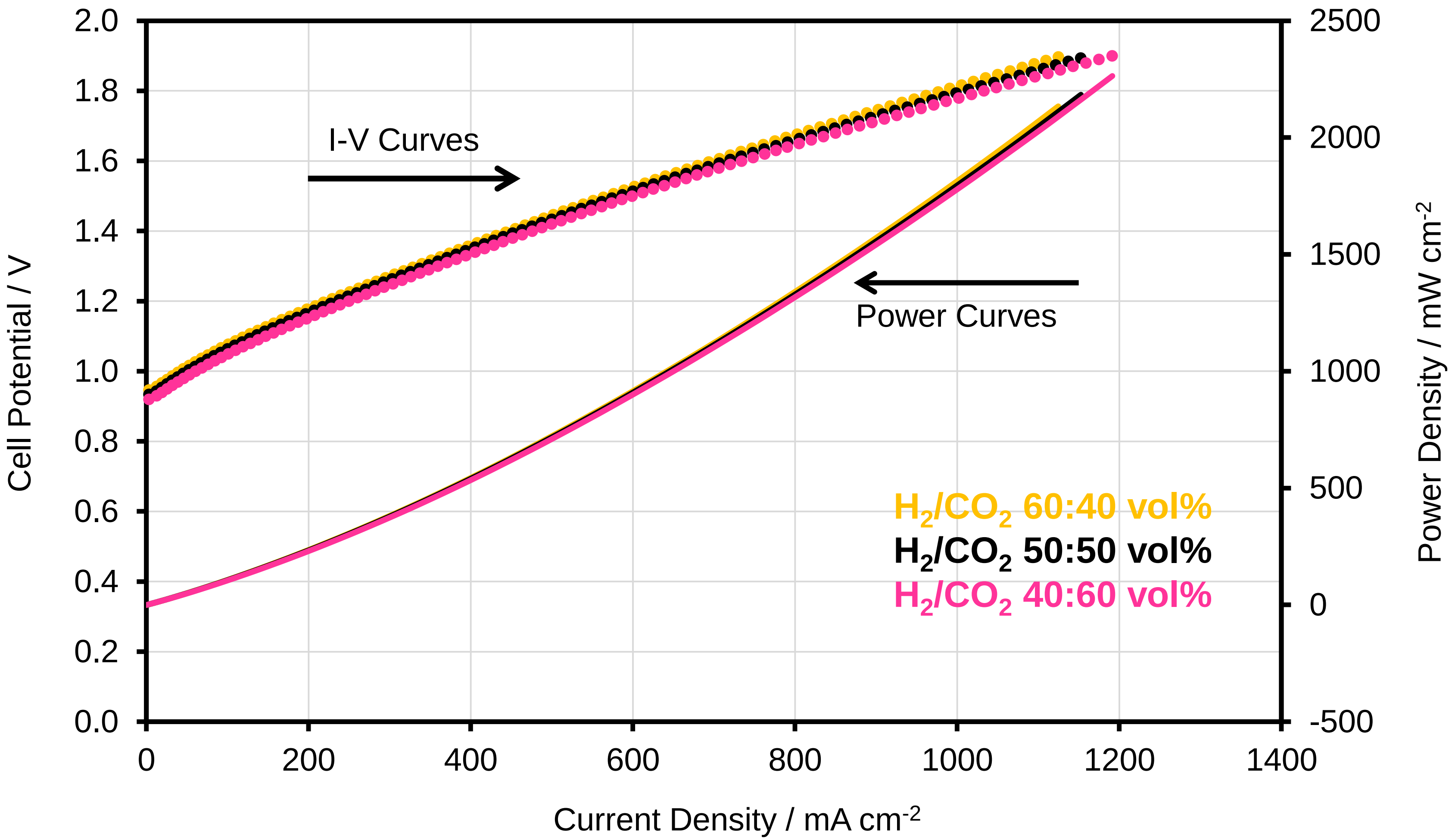
Activation losses increase as the CO_2 content is decreased

No concentration losses observed

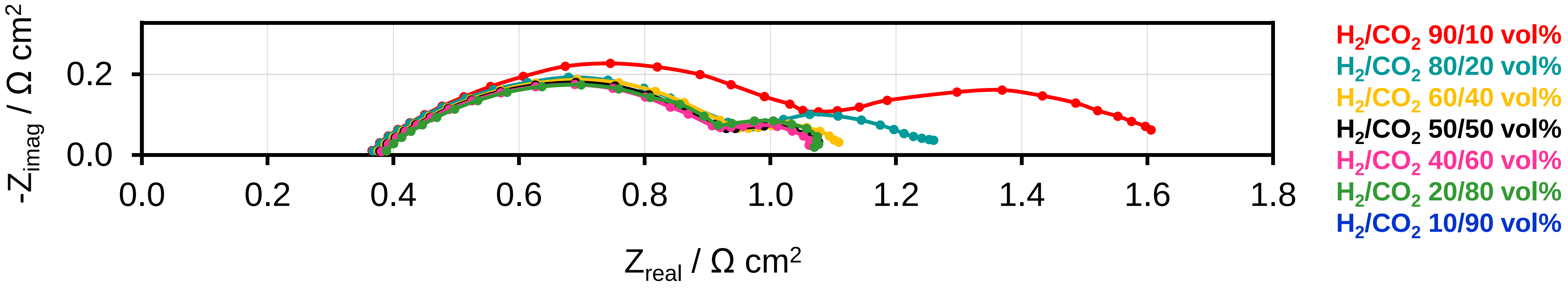


I-V Curve Measurements

Cell performance and power input not significantly affected by fuel variability within the range 40-60 vol% H_2



Electrolysis Mode Impedance



Low frequency arc width increases when CO_2 < 40 vol%: increased diffusion losses[6] over this composition range

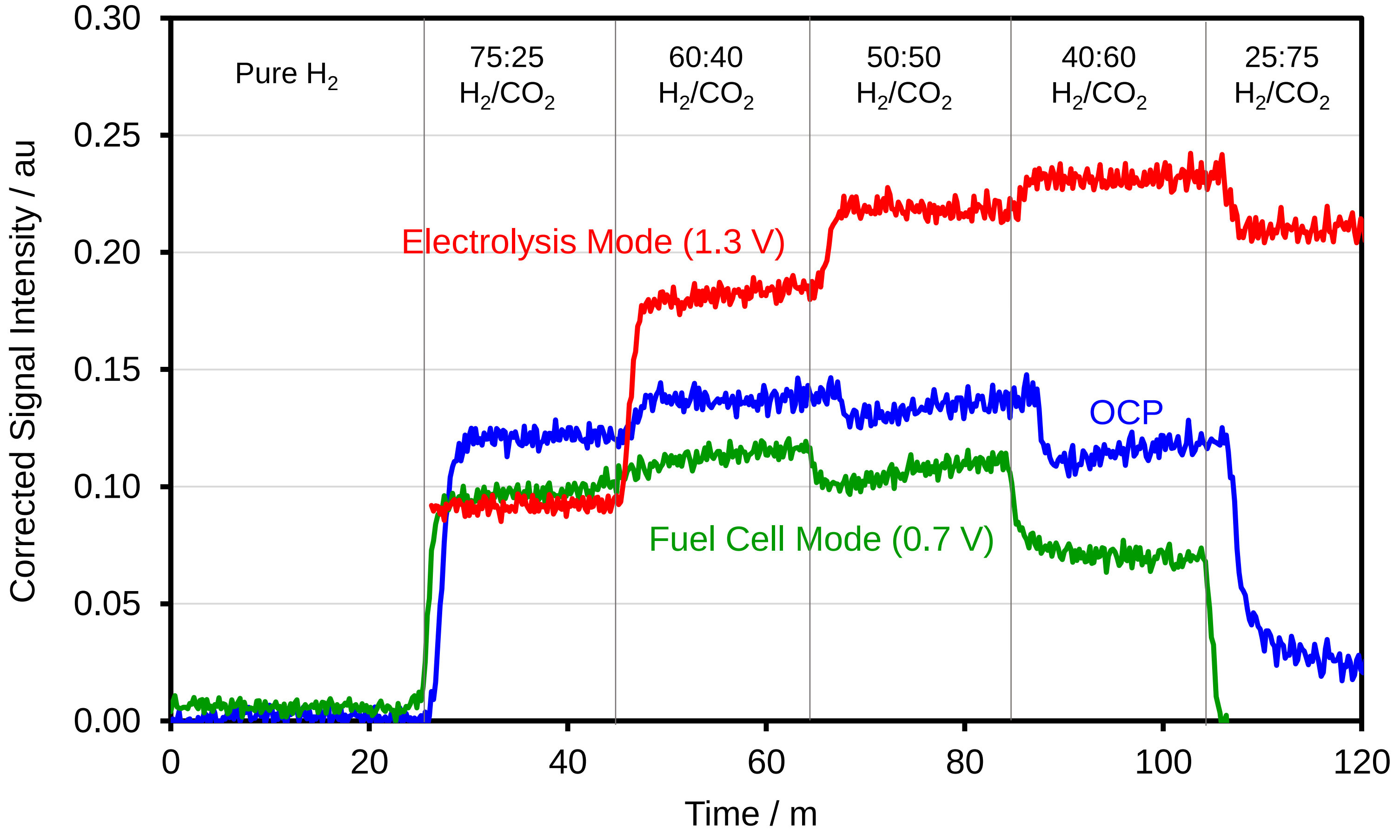
High frequency arc width increases with decreasing CO_2 content: H_2O and CO_2 are electrochemically[6] reduced to produce H_2 and CO respectively

H_2/CO_2 vol%	High Frequency Arc Width / Ω cm^2	Low Frequency Arc Width / Ω cm^2
90:10	0.7105	0.5290
80:20	0.5880	0.3039
60:40	0.5887	0.1444
50:50	0.5514	0.1460
40:60	0.5392	0.1415
20:80	0.5276	0.1530

[6]Zhan *et al*. Energy Fuels 23 (2009) 3089-3096.

CO Production

CO production decreases when CO_2 > 60 vol%, indicating production is enhanced by the RWGS reaction



Electrolysis Mode – 50/50 vol% H_2/CO_2

Reverse Water-Gas Shift:

$H_2 + CO_2 \rightleftharpoons H_2O + CO$

Hydrogen Production:

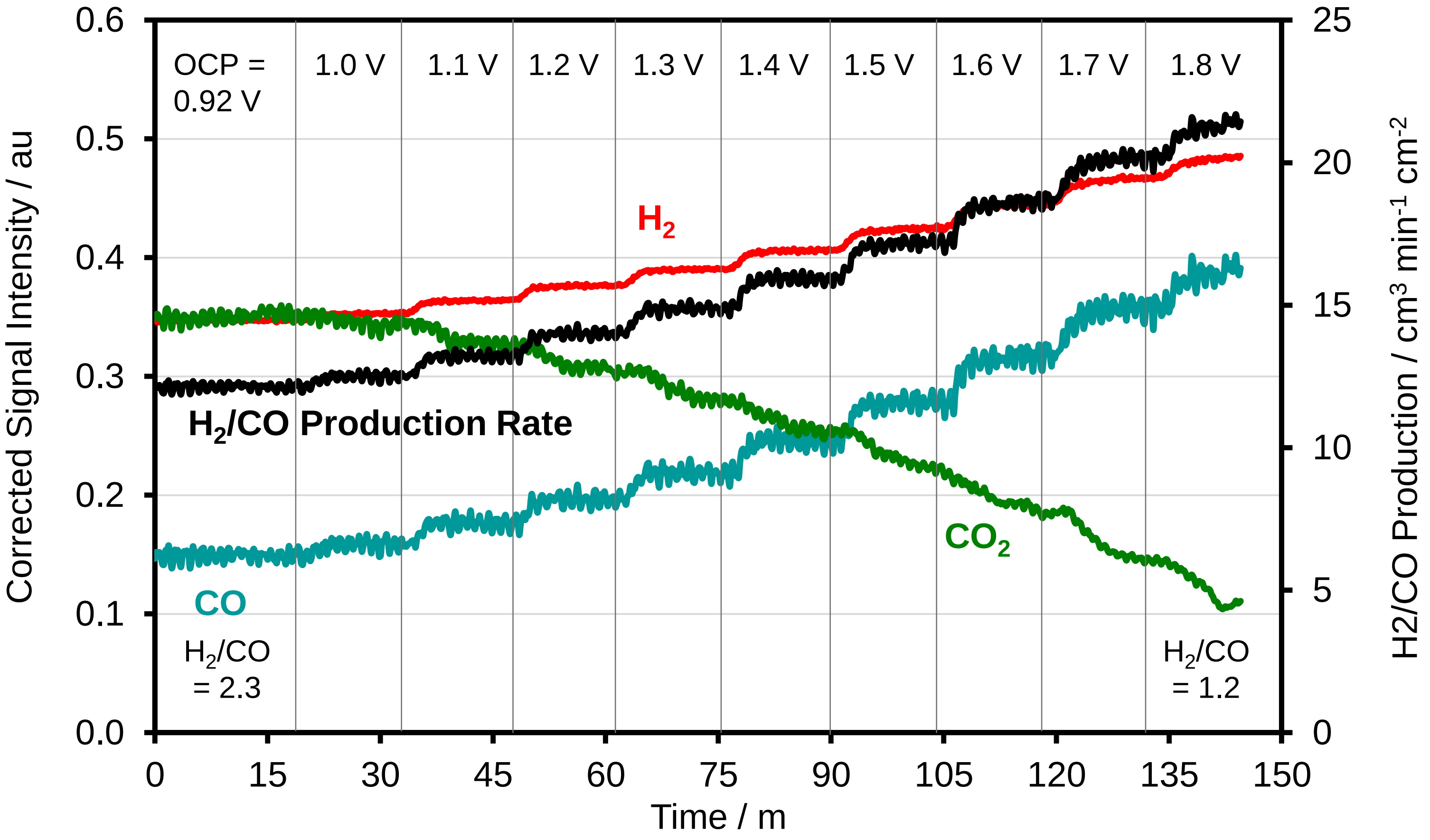
$H_2O + 2e^- \rightleftharpoons H_2 + O^{2-}$

CO Production:

$CO_2 + 2e^- \rightleftharpoons CO + O^{2-}$

and

$H_2 + CO_2 \rightleftharpoons H_2O + CO$



Conclusions

- SOFCs can utilise H_2/CO_2 mixtures in fuel cell mode to yield electrical power and heat, or electrolysis mode to yield synthesis gas mixtures (H_2/CO)
- Performance and fuel processing are sensitive to fuel composition and variability, but are not significantly affected provided the H_2/CO_2 composition stays within 40-60 vol% H_2
- In fuel cell mode, power production is predominantly through electrochemical H_2 oxidation, whilst CO is converted in the WGS reaction and makes negligible contribution to power production
- In electrolysis mode, CO production is through a mixture of the RWGS reaction and electrochemical CO_2 reduction, while H_2 is regenerated via electrochemical H_2O reduction

Acknowledgements

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- FLEXIS is part-funded by the European Regional Development Fund (ERDF), through the Welsh Government / Ariennir yn rhannol gan Gronfa Datblygu Rhanbarthol Ewrop drwy Lywodraeth Cymru