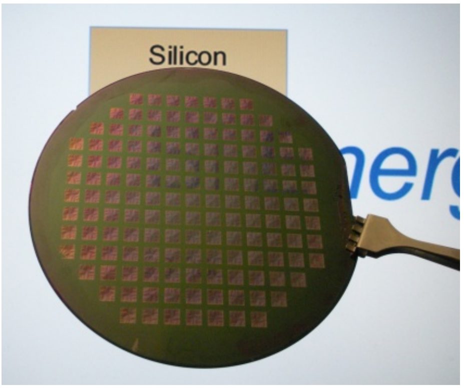
Silicon 14 Si Energy Systems, LLC
An Allied Minds Company

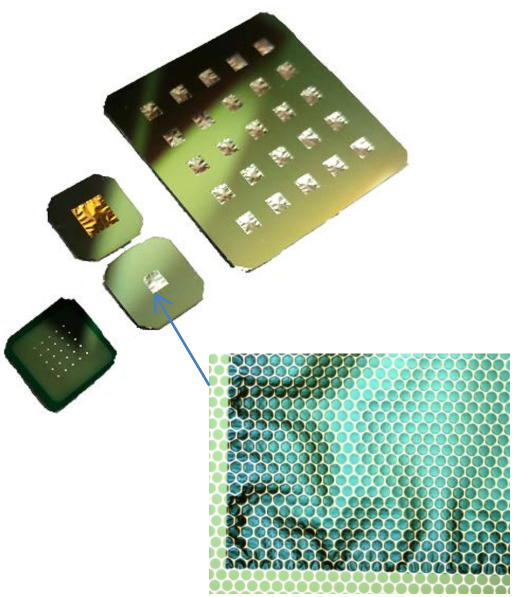
HARVARD UNIVERSITY

Direct Hydrocarbon Fuel Cell – Battery Hybrid Electrochemical Device

Project PI: Masaru Tsuchiya
Co-PIs: Prof Shriram Ramanathan and Prof Cynthia Friend

About SiEnergy Systems

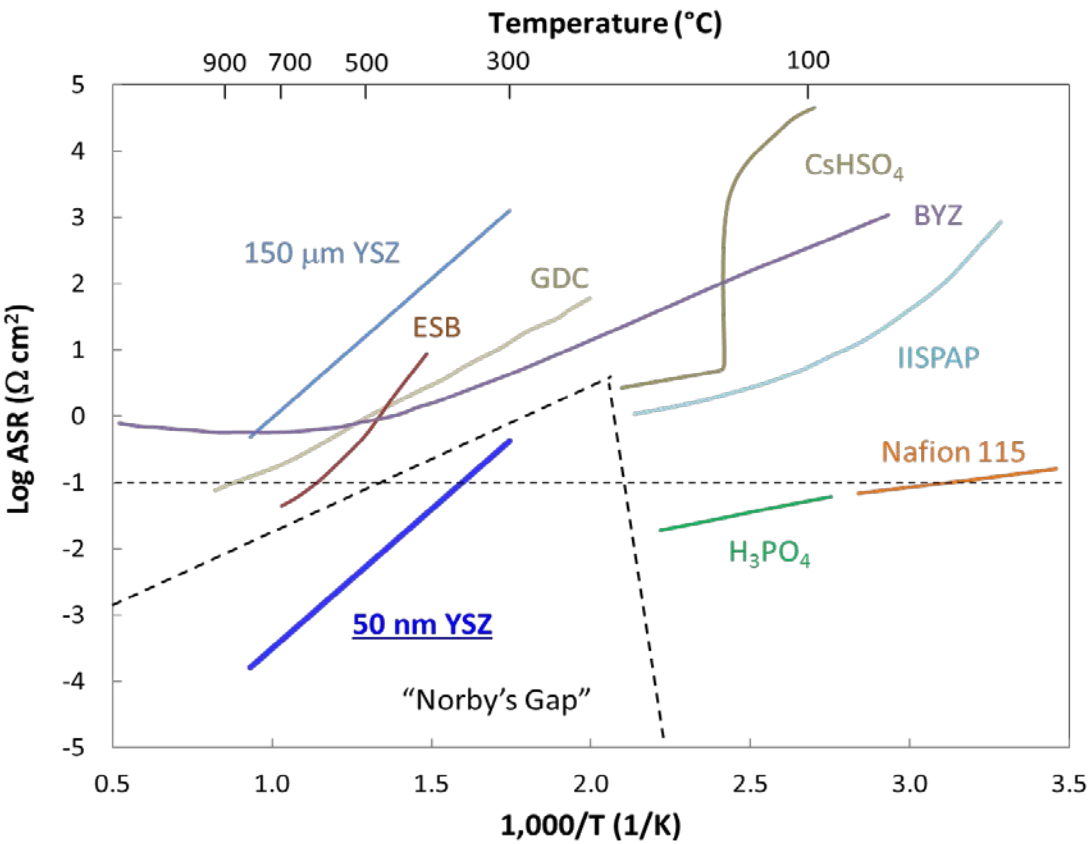


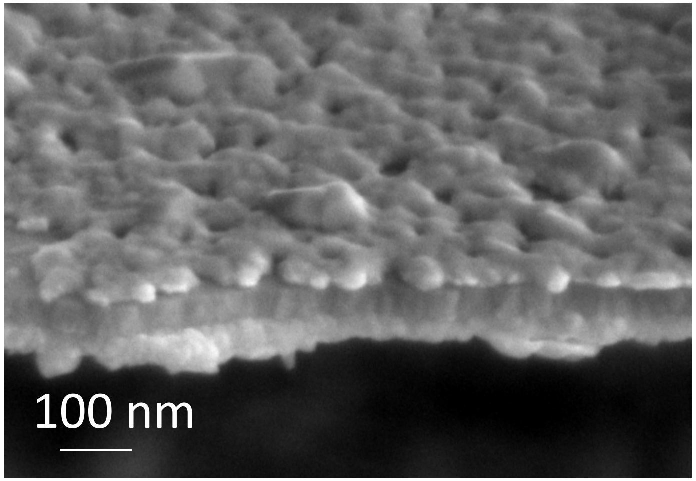


- SiEnergy was formed in 2007 by Allied Minds (LSE: ALM), an innovative U.S. science and technology development and commercialization company.
- The technology was originally based on the research of Professor Ramanathan of Harvard University.
- In the period from 2007 to 2010, SiEnergy worked through an SRA with Harvard.
- Scalability of core technology (ultra-thin film SOFC) was demonstrated in 2010.
- SiEnergy moved to its own facility in Cambridge in 2011, and expanded R&D team in 2012.
- ARPA-E REBELS program to develop dual-mode device started in 2014.

Ultra-thin film SOFC

Platform to demonstrate fuel cell at 300-500 °C





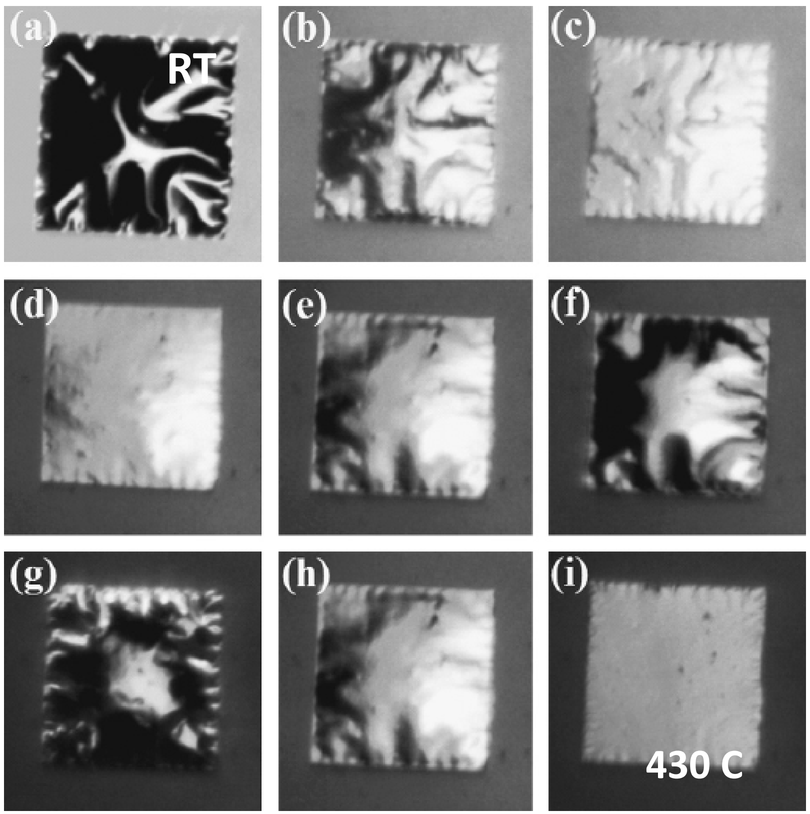
M. Tsuchiya *et al.*,
Nature Nanotechnology, 6, 282 (2011).

- Area specific resistance (ASR) of 50 nm YSZ is only 0.005 Ωcm^2 at 500 °C.
- Thin film YSZ is often required for new electrolyte materials as blocking layer.
  → *Nanoscale YSZ provides the lowest practically achievable resistance for 300-500 °C.*

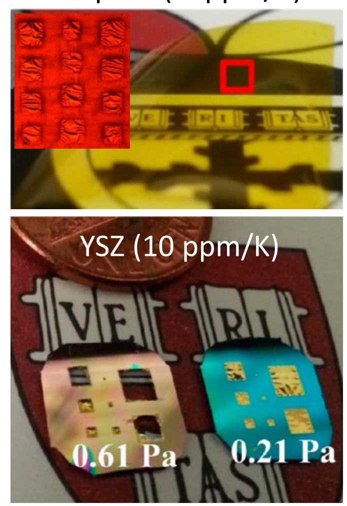
ASR was calculated for 150 μm membrane, except Nafion 115 (127 μm) and 50 nm YSZ

Key advantage of thin-film deposition for SOFC fabrication

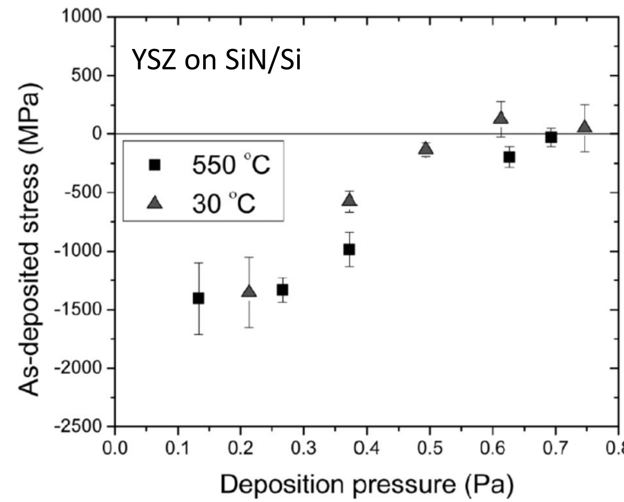
Ease of integration of dissimilar materials (i.e., flexible materials selection)



Kapton (20ppm/K)



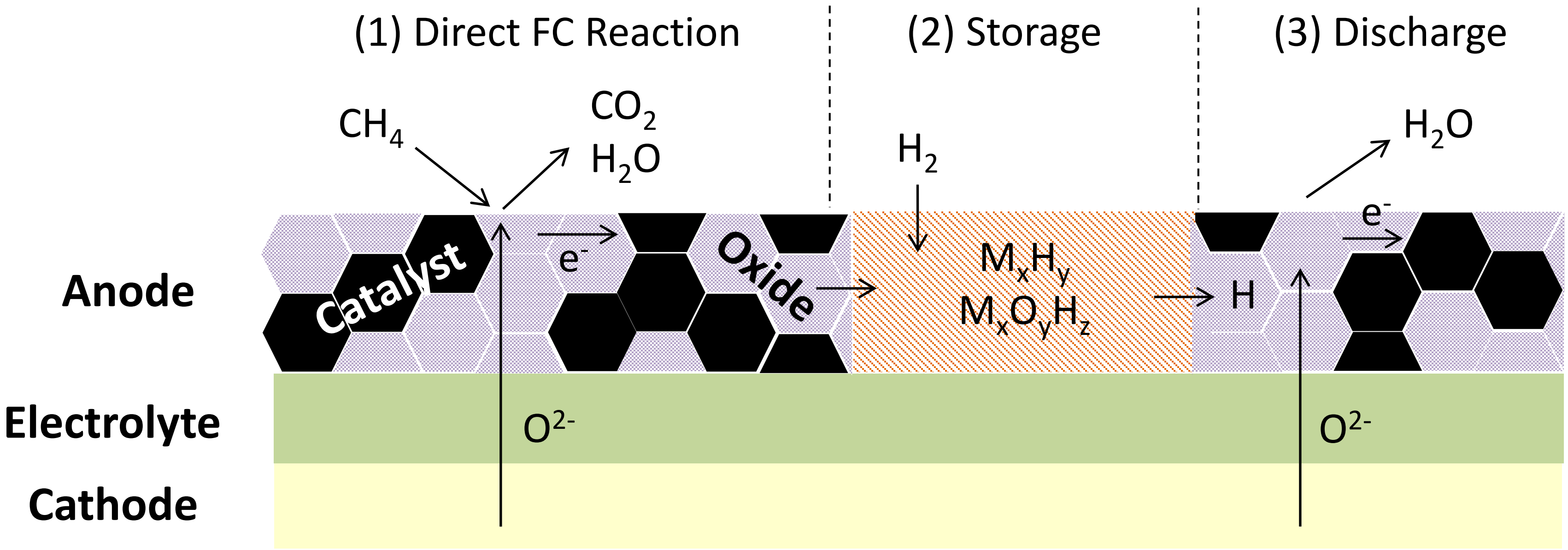
Silicon (4 ppm/K)



- Initial stress can be tuned by process conditions to counter-balance thermal stress applied during heating/cooling.

B. K. Lai, S. Ramanathan *et al.*, J. Power Sources, **195**, 5185 (2010).
K. Kerman, S. Ramanathan *et al.*, ACS Nano, **7**(12), 10895 (2013).

Technology Overview

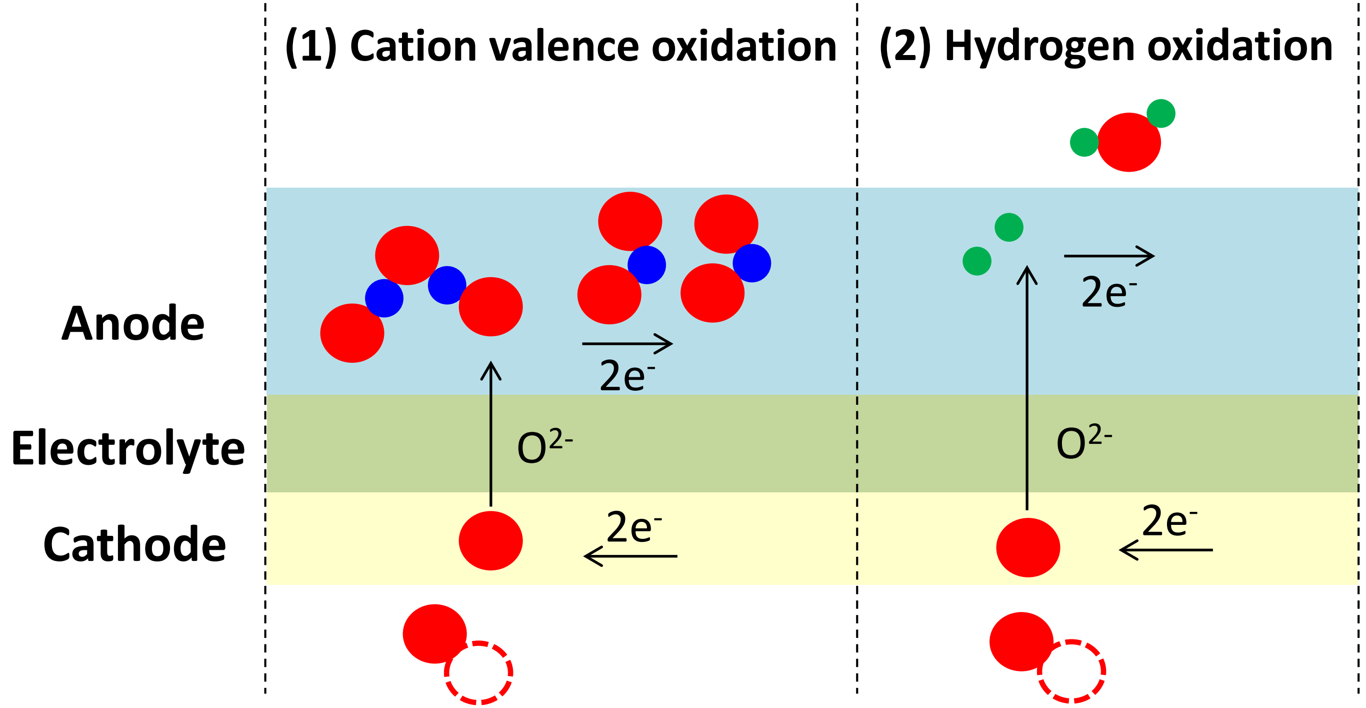


<u>**Key novelties of the proposed project**</u>

- ***In-situ* charge storage in anode to enable battery-like transient response**
  - Transition metal oxide and/or metal hydride to store hydrogen
- **Direct hydrocarbon operation to avoid the use of fuel processing units**
  - Carbide catalyst to activate C-H bond at low temperature

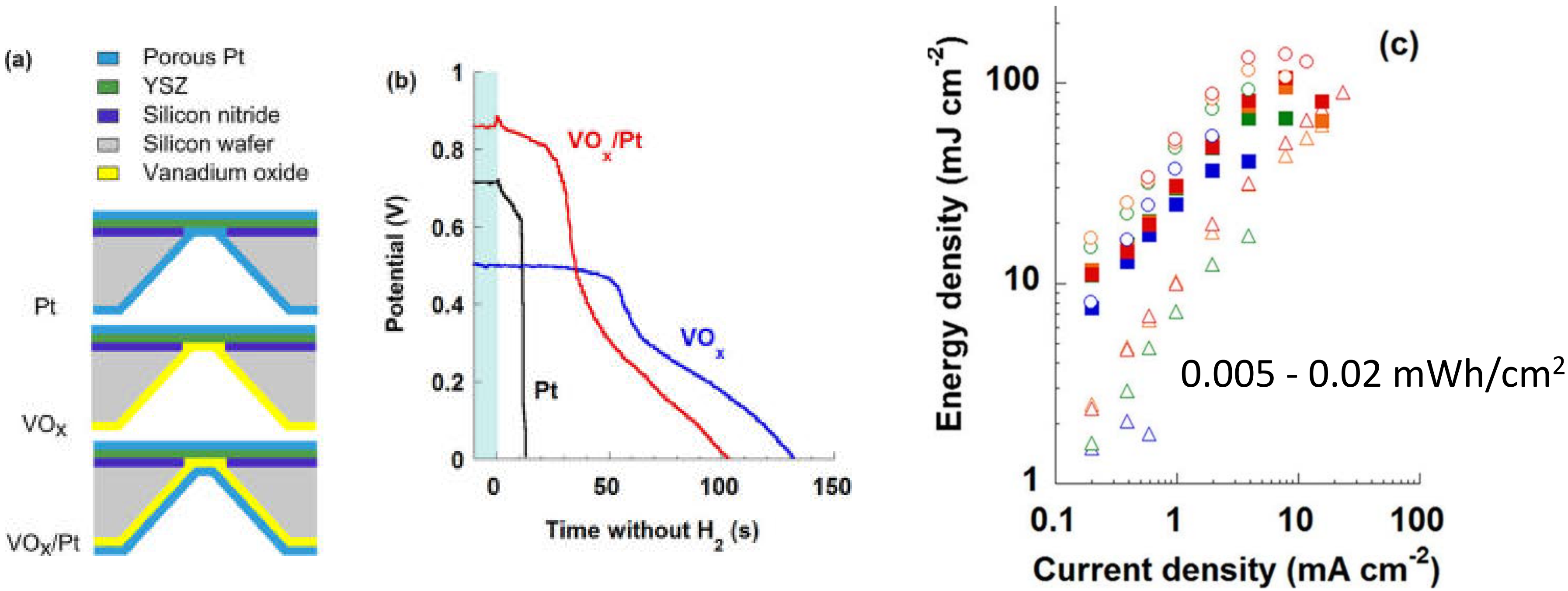
In-situ charge storage in anode

Possible mechanisms for *in-situ* charge storage



- So far, *in-situ* storage was observed in a few transition metal oxides.
- The most likely mechanisms for the in-situ storage are the following.
  - Cation valence oxidation (such as VO_2/V_2O_5)
  - Hydrogen storage (Hydrides with H/V ratio 0.3-1.2 were reported)

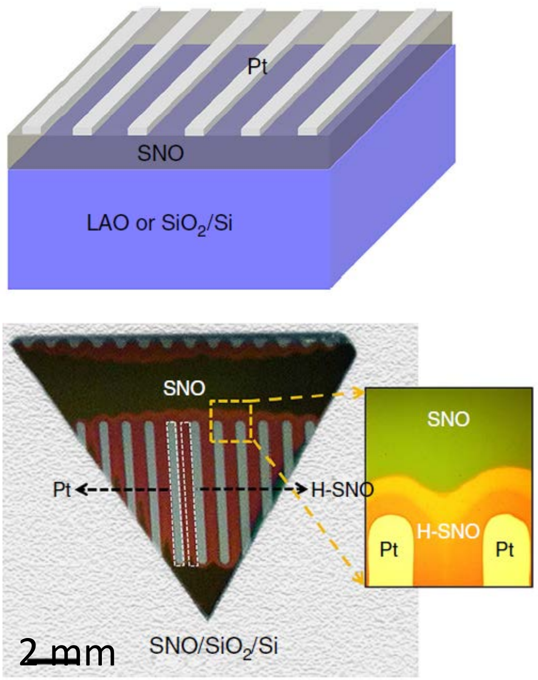
Battery-like response in VO_2 film

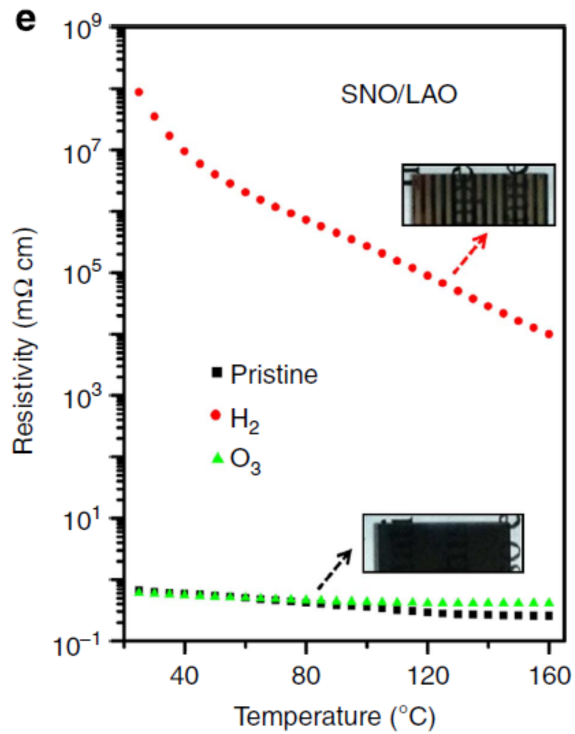


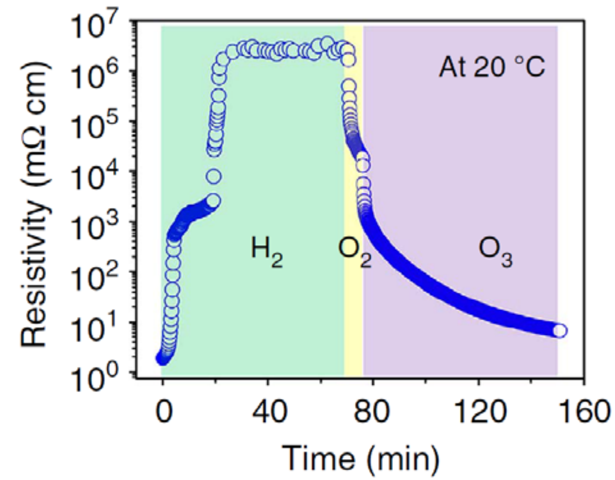
- Testing was performed at 300 °C using ultra-thin film YSZ platform.
- V^{4+} to V^{5+} transition observed in vanadia film after battery mode operation.
- Energy density was 20-100 mJ/cm^2 (0.005-0.02 Wh/cm^2) tested at 0.1-10 mA/cm^2.

Q. V. Overmeere, S. Ramanathan *et al.*, Nano Lett., 12 (7), 3756–3760 (2012).

Hydrogen intercalation in $SmNiO_3$ thin film







Resistivity and optical properties of perovskite oxide (nickelate) can be tuned by several orders of magnitude by doping hydrogen.

J. Shi, Y Zhou, and S. Ramanathan, Nature Communications, **5**, 4860 (2014).

Direct hydrocarbon operation at 300-500°C with carbide catalyst

Transition metal carbide catalyst for direct hydrocarbon oxidation at 300-500°C

Catalyst development is necessary to operate SOFCs with hydrocarbon fuels at 300-500 °C

- Steam reforming is not favorable below 650 °C.
- Coking is a major challenge with Nickel catalyst.

Transition Metal Carbide Catalyst

- Catalytic properties similar to Pt-group metals. [1]
- High electronic conductivity comparable to metals.
- Resistant to coarsening due to very high melting point (e.g., WC: 2870 °C).
- Resistant to coking demonstrated in direct methane SOFC.[2]

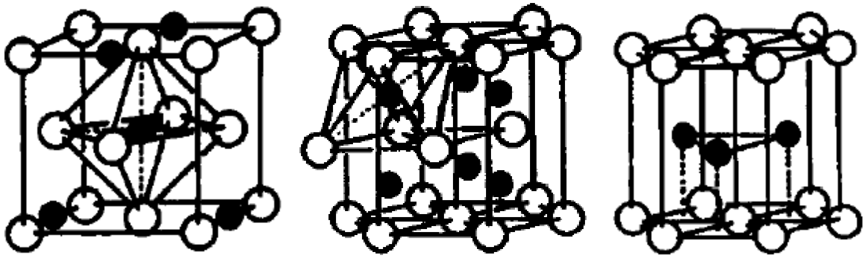
[1] S. T. Oyama, *The Chemistry of Transition Metal Carbides and Nitrides*, Chapman & Hall (1996).

[2] Torabi and Etsel, J. Electrochem. Soc., 159(6), B714 (2012).

Structure of carbides (bulk and thin film)

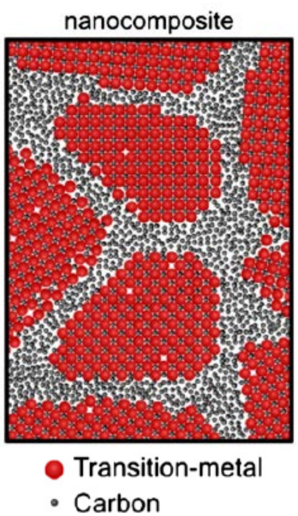
Crystal structure of carbide [1]

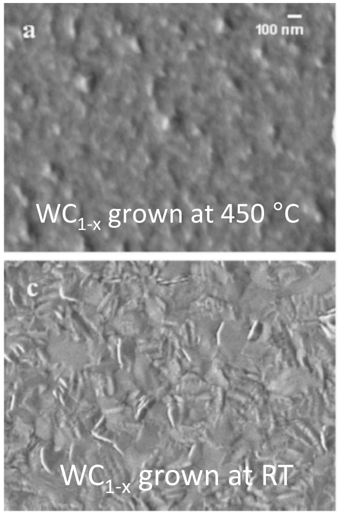
FCC | HCP | Simple Hex.



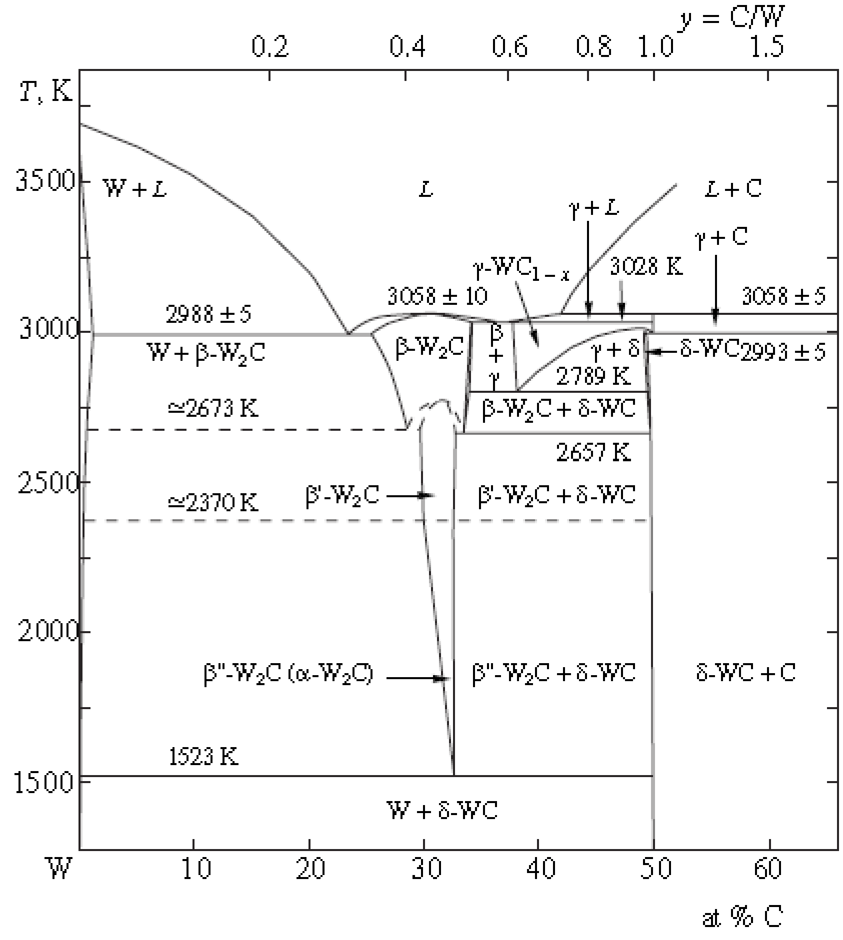
WC_{1-x}, MoC_{1-x} | W_2C, Mo_2C | WC, MoC

Structure of sputtered WC [2,3]



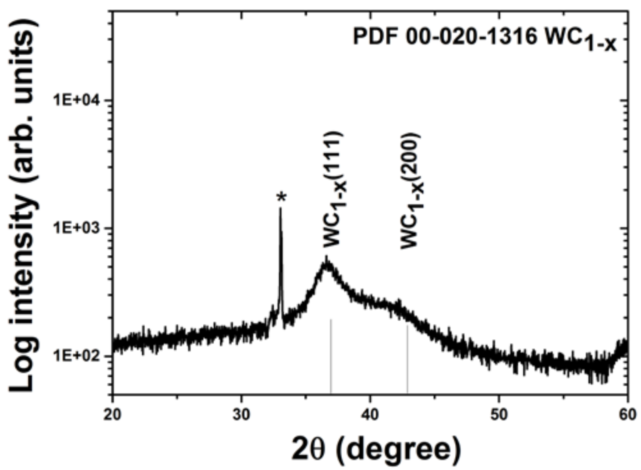


W-C Phase Diagram [4]



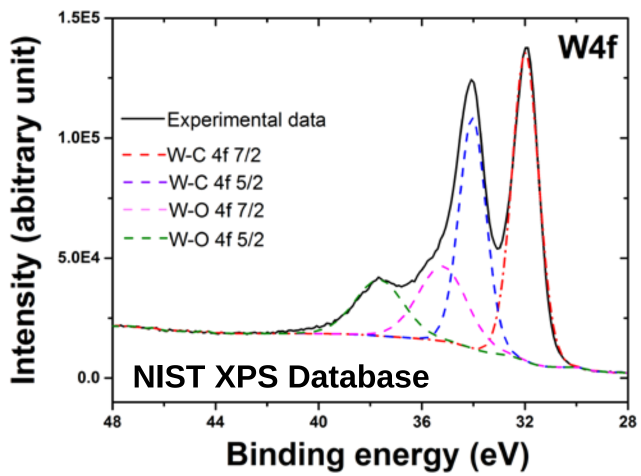
[1] S. T. Oyama, Catalysis Today, **15**, 179-200 (1992).
[2] Jansson *et al.*, Thin Solid Films, **536**, 1 (2013).
[3] Weigert et al., J. Vac. Sci. Tech A, **26**,23 (2008).
[4] Kurlov and Gusev, Inorg Mater, 42(2), 121 (2006).

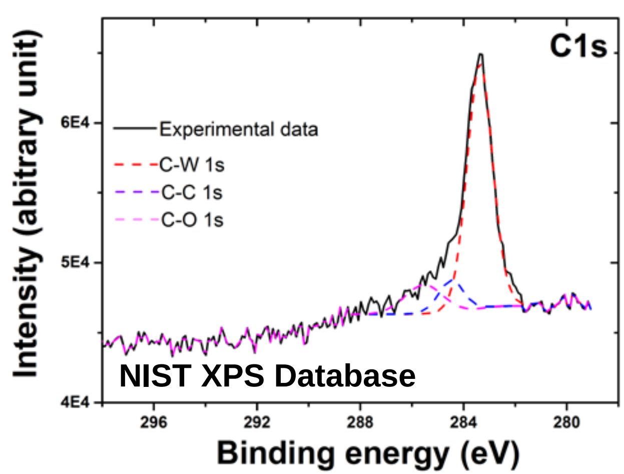
Thin film WC is nonstoichiometric (WC_{1-x})



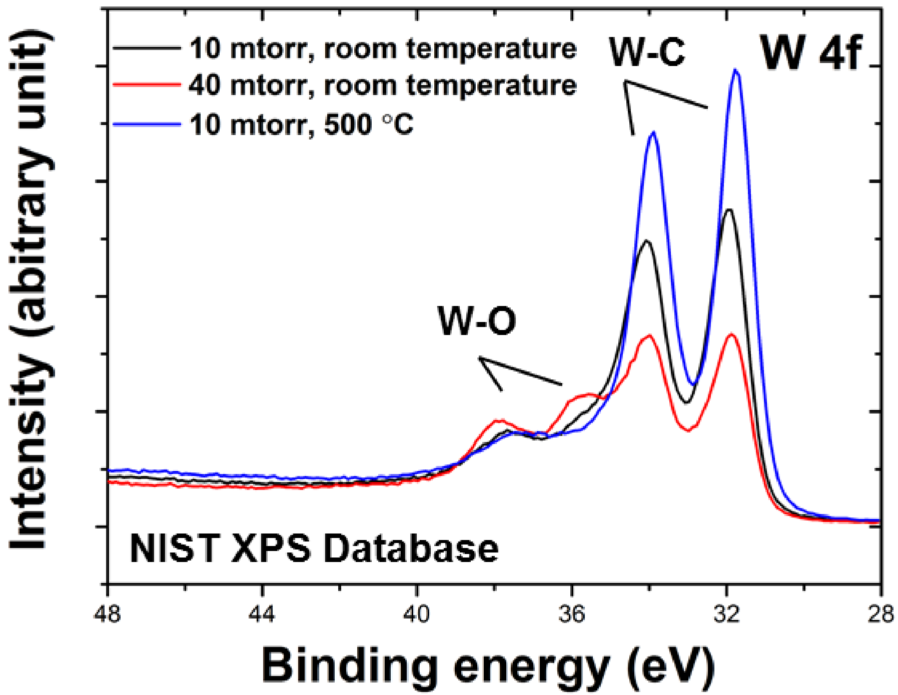
- **WC thin films prepared at 150 W, 10 mtorr and room temperature were found to be mainly (111) oriented WC_{1-x} (PDF 00-020-1316);**

- **W4f and C 1s confirm WC's existence;**





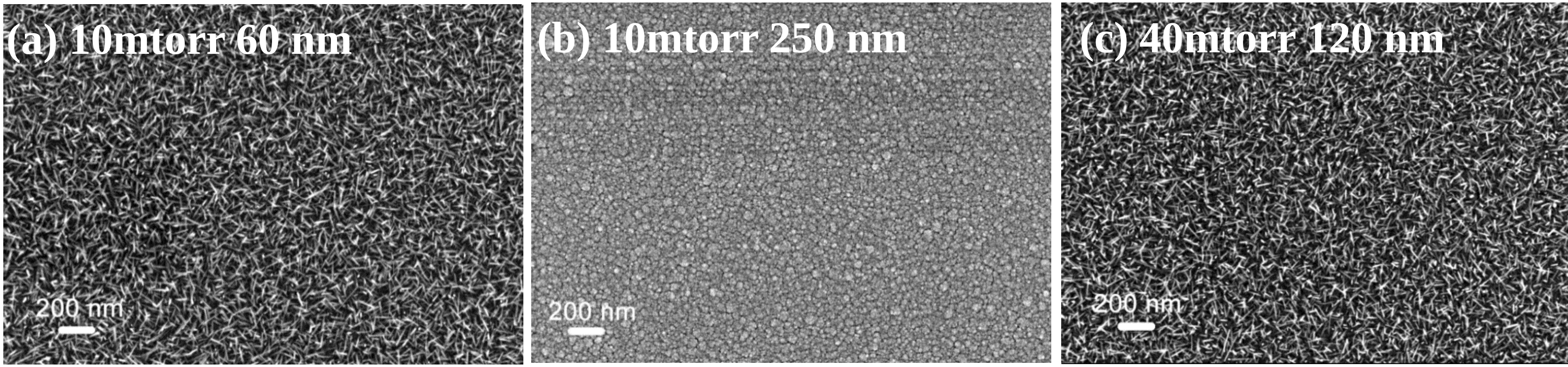
Composition of WC is very sensitive to the growth conditions



- W-C intensity increases with deposition temperature, while decrease with deposition pressure;
- W-O intensity increase with deposition pressure;

Challenges in using carbide in CH_4

WC was annealed in pure CH_4 under 500 ˚C for 4 h



- Unlike noble metal or oxide anodes, oxidation is a key challenge to use of WC as anode;
- The possible oxide products include WO_2, WO_3, and $W_{18}O_{49}$;
- Doping, and control of defects and interfaces can mitigate these issues.

Summary

- Nanoscale thin film electrolyte is an excellent platform to lower the operating temperature of solid oxide fuel cells down to 300-500 °C.
- *In-situ* charge storage in anode was demonstrated by integrating transition metal oxide in anode.
- Transition metal carbide catalyst has been investigated as a catalyst to activate C-H bond at below 650 °C.

Acknowledgements

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