Solid Oxide Fuel Cells and Electrolysers

Solid State Ionics 2024

CLEAN ENERGY STARTS WITH CERES

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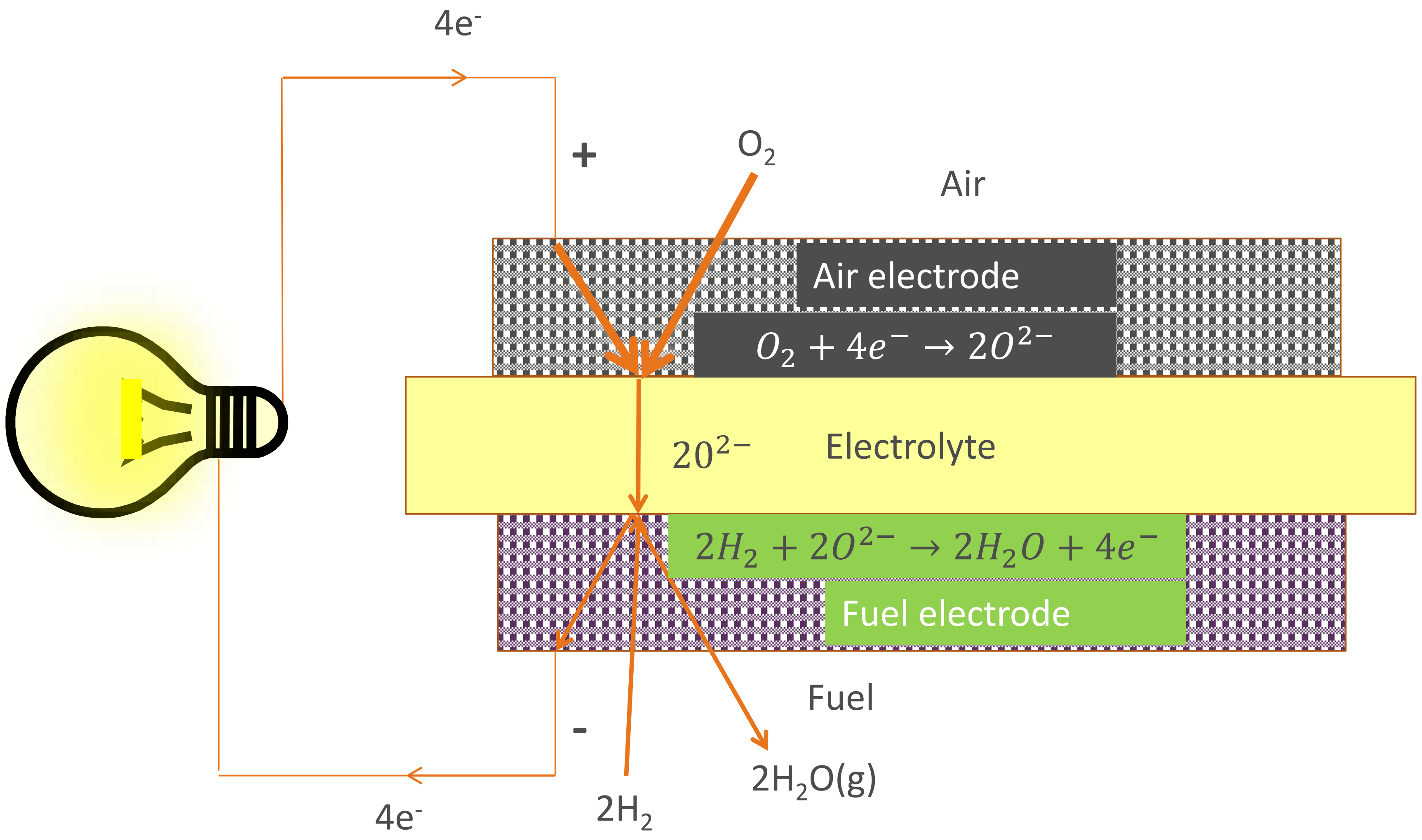
Contents

Introduction

- Title of tutorial in the program is 'Fuel Cells and Electrolysers'
- A number of technologies exist in this field operating at a range of temperatures between ambient and 500°C+
  - Proton exchange membrane (ambient to 200°C)
  - Alkaline (ambient to 90°C)
  - Molten carbonate (600°C +)
  - Solid oxide (500°C +)
- The tutorial will be limited to Solid Oxide Cell (SOC) technology where the electrolyte is a solid state ionic conductor due to time constraints
  - The mature technology uses oxygen ion conducting electrolytes which are being actively commercialised
  - Proton-conducting electrolytes also exist but the technology is less mature and fundamental materials science issues need to be addressed before this can be matured

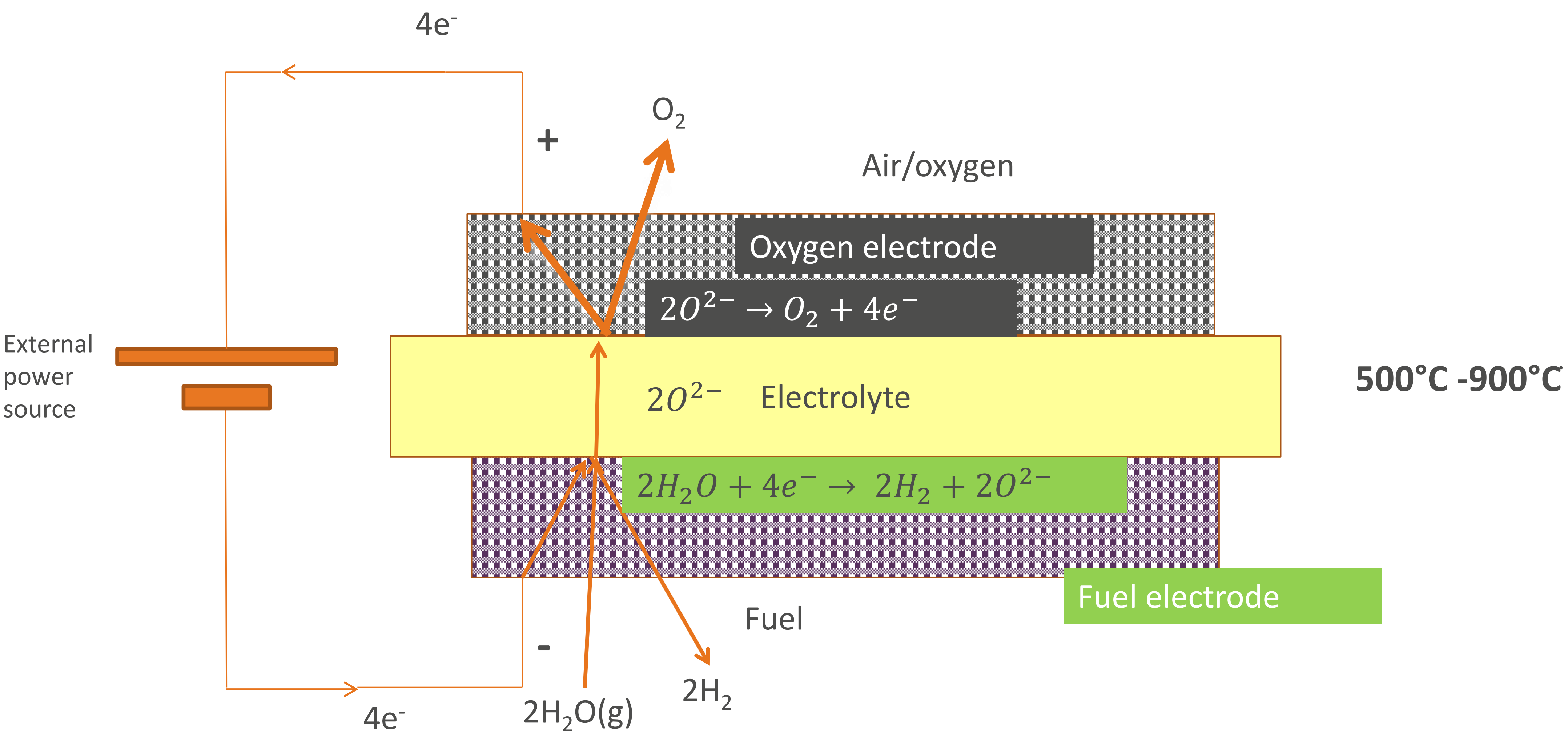
SOC fundamentals

Solid oxide cell fundamental principles (fuel cell mode -SOFC)



500°C -900°C

Solid oxide cell fundamental principles (electrolysis mode -SOEC)



Why fuel cells?

- Theoretical efficiency of fuel cell system (conversion of chemical to electrical energy)
  - Hydrogen fuelling 82.6%
  - Methane (natural gas) fuelling 99.8%
- Theoretical efficiency not achievable in practice as with heat engines, but 50-65% efficiency practically achievable on natural gas fuelling (for an SOFC)
  - Very high efficiency possible at small scale (700W SOFC system has similar efficiency to state of the art 500MW power station).
  - Efficiency of >60% possible at >5kW_e scale
  - Small heat engines generally very inefficient…
- High efficiency…. Low CO_2 emissions
- SOFC systems now deployed at scales up to 1MW
- Low secondary pollutants…. Clean air

Why SOEC for electrolysis?

- Steam splitting requires less electrical energy than water splitting (provided a source of heat is available)
  - $H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)\ \Delta H_{298K} = \mathbf{242kJ.mol^{-1}}$
  - $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)\ \Delta H_{298K} = \mathbf{286kJ.mol^{-1}}$
- Typically >90% of the cost of hydrogen produced through electrolysis is electrical energy, so this is a significant cost saving
- Process integration with other industrial processes with waste heat available: decarbonisation of 'hard to abate' industries where direct electrification is not possible
  - Ammonia plants
  - Steel plants
  - Chemical plants

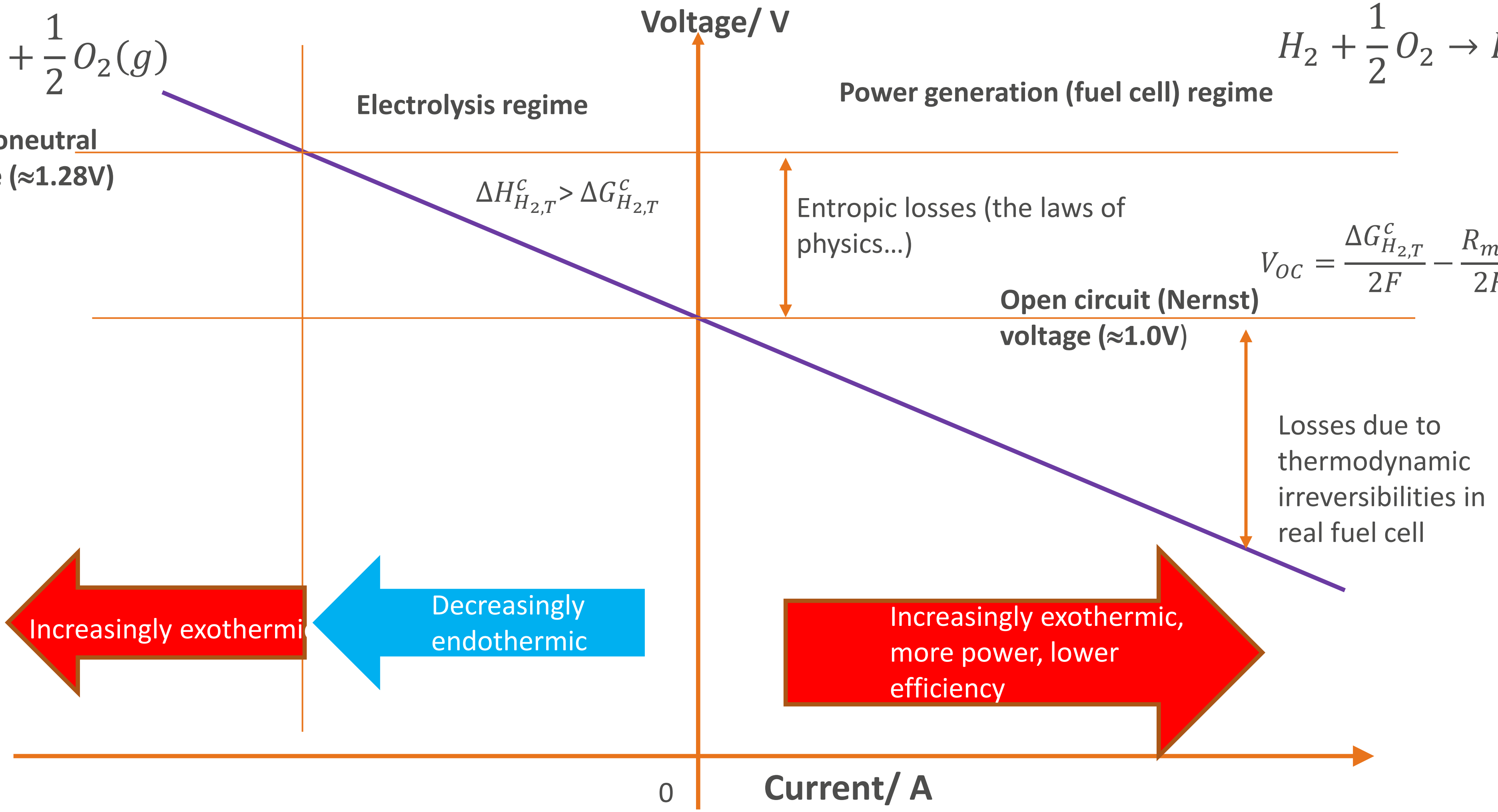
Current voltage curves for SOCs

$$H_2O(g) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g)$$

$$V_{TN} = \frac{\Delta H^c_{H2,T}}{2F}$$ Thermoneutral voltage (≈1.28V)

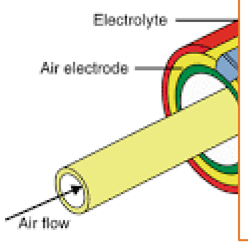
$$V_{OC} = \frac{\Delta G^c_{H2,T}}{2F} - \frac{R_m T}{2F}\ln\left(\frac{p_{H2O}}{p_{H2}p_{O2}^{0.5}}\right)$$



Types of SOC

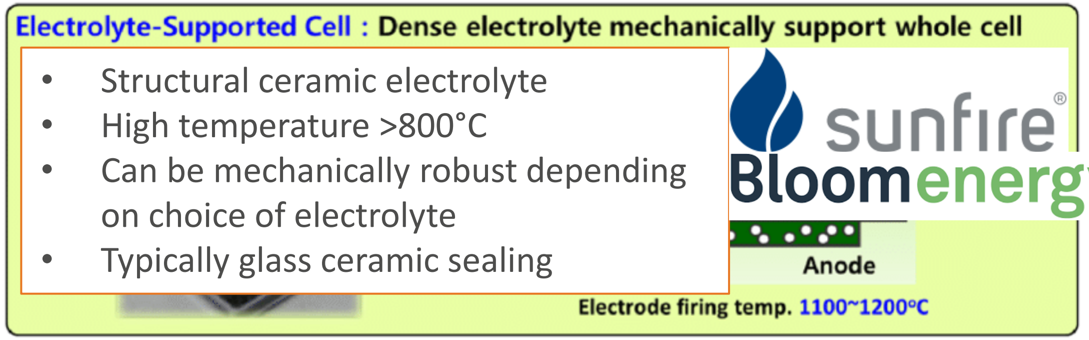
SOC cell designs

Tubular



- Mechanically robust
- Typically high temperature >850°C
- Poor volumetric power density

Electrolyte supported planar

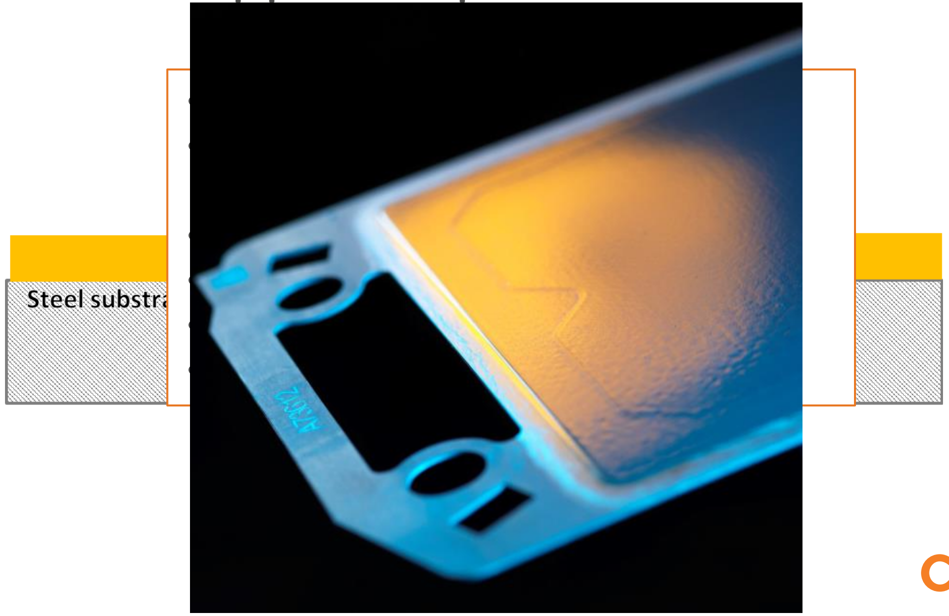


- Structural ceramic electrolyte
- High temperature >800°C
- Can be mechanically robust depending on choice of electrolyte
- Typically glass ceramic sealing

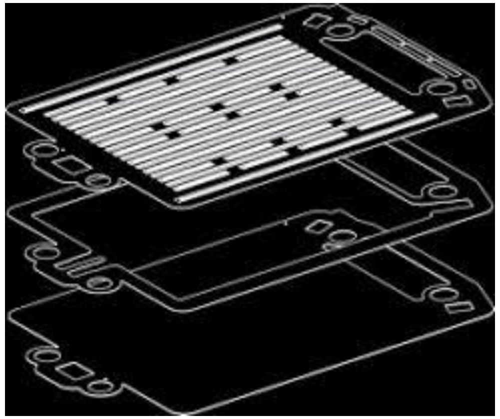
Fuel electrode supported planar

- Structural cermet fuel electrode
- Thick film electrolyte
- Intermediate temperature 600-800°C
- Challenges with mechanical robustness
- Typically glass ceramic sealing

Metal supported planar



Stacking to achieve usable power (planar cells)



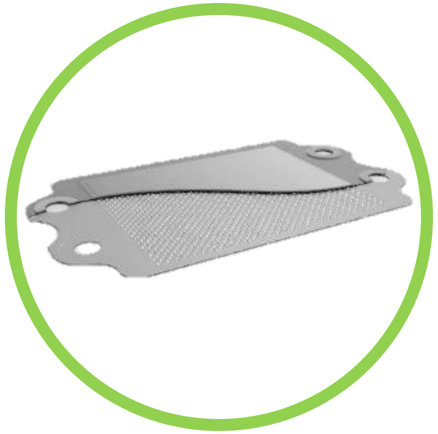
elcoStack

elcoStack® E3000 (3kW)

- Connect multiple cells electrically in series to boost voltage and power to usable level (usually >50)
- Supply fuel to fuel electrode and air to air electrode without allowing them to mix (normally in parallel)
- Maintain electrical isolation between adjacent cells
- Power connection at top and bottom of stack
- Facilitate thermal management
- Usually use stainless steel interconnect (bipolar) plates to separate reactants between adjacent cells

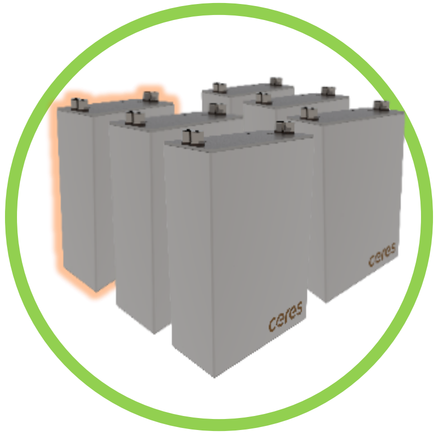
Modular scale-up concept for green hydrogen

Cell
30-150W

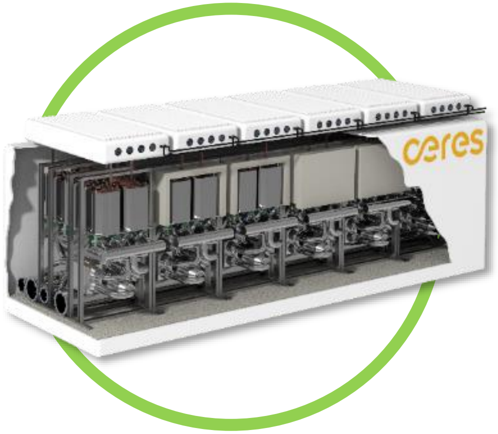


Stack
10-50 kW

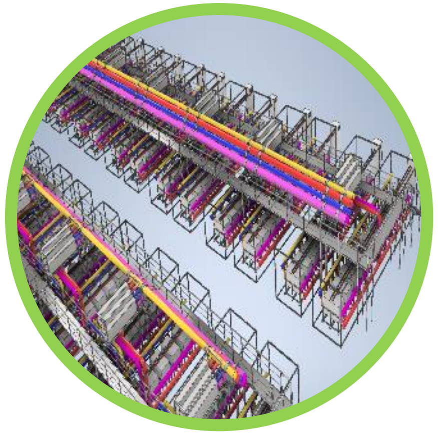
Stack array
100-500 kW



Module
1-5 MW



Plant
100MW-GW



Industrial de-carbonisation of green steel, green ammonia, e-fuels. Chemicals, oil and gas.

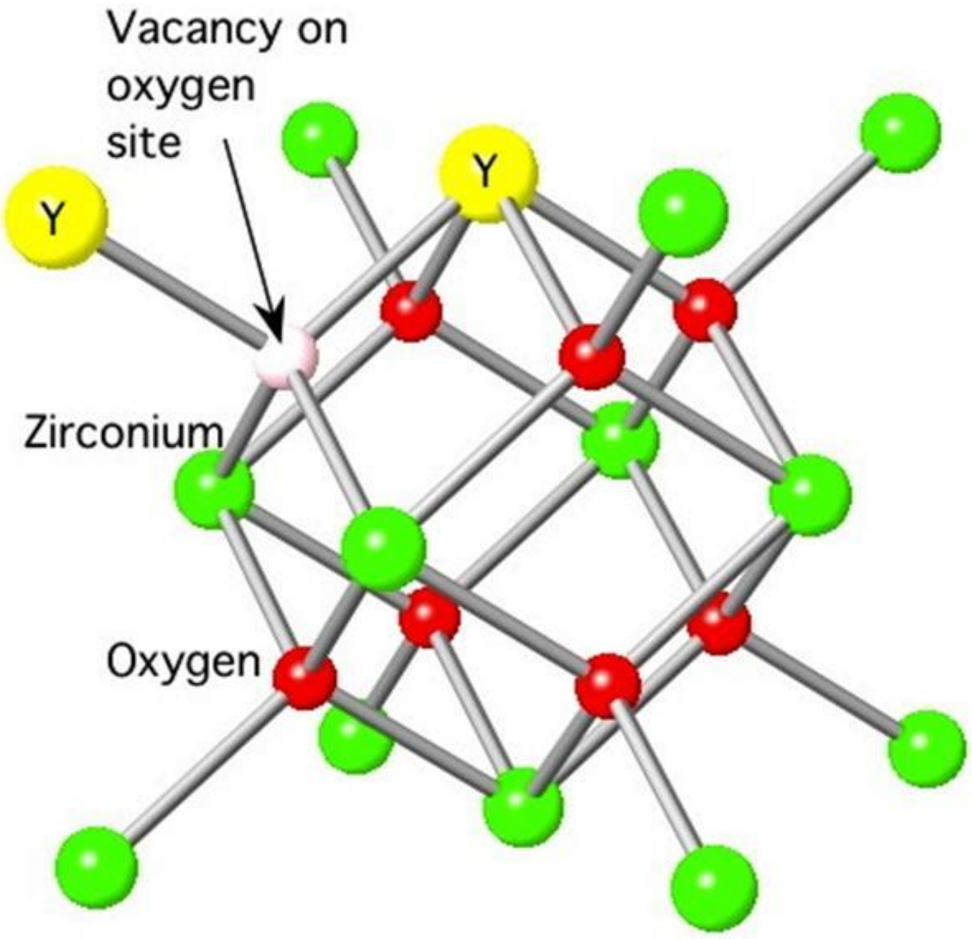
SOC Materials: Electrolytes

Electrolytes: the Solid Oxide in Solid Oxide Cells

- Electrolytes are fundamental to the functioning of the cell
  - Metal oxides where oxide ions (O^{2-}) can move through the crystal structure if a chemical potential gradient of oxygen is applied
    - Since oxygen ions are charged, this allows an electric current to flow through the electrolyte, using oxide ions rather than electrons as the charge carriers
  - Electrolyte materials need to
    - Conduct oxygen ions (usually only at elevated temperatures, all practical electrolytes are essentially insulating at ambient temperature)
    - NOT conduct electrons (otherwise the cell will internally short)
    - Not react with other cell materials or fuel/ air constituents
    - Be capable of forming dense gas-tight layers

Electrolytes: Doped zirconia and doped ceria- the cubic fluorites

- Used in the vast majority of SOCs
- Electrolyte materials based on zirconium oxide (zirconia) ZrO or cerium oxide (ceria) CeO_2, both have the cub t conduct oxygen ions
  - Both cerium and zirconiur
  - By doping the ceria or zirc example yttrium oxide) to form a mixed oxide, vacar rm in the crystal structure
  - This allows the material tc oxygen ions can hop from vacancy to vacancy throug



Electrolytes: Zirconia

- Zirconia-based electrolytes are by far the most common in SOCs (also used in λ-sensors in car exhausts, which are really tubular SOCs).
  - Zirconia desirable attributes
    - Very chemically stable
    - Reasonable ionic conductivity at >650°C
    - Negligible electronic conductivity
    - Reasonable mechanical properties for a ceramic
    - Easy to sinter to high density (start with powder and end up with a porosity-free ceramic), but requires temperatures >1300°C
  - Yttria-stabilised zirconia (YSZ) is the most common variant
    - For SOC use 8YSZ $(ZrO_2)_{0.92}$ $(Y_2O_3)_{0.08}$ is the most common material as it has the highest ionic conductivity at >650°C
  - Scandia-stabilised zirconia (ScSZ) has higher ionic conductivity, but scandium is expensive
    - Often co-stabilised eg 10Sc1YSZ $(ZrO_2)_{0.89}$ $(Sc_2O_3)_{0.1}$ $(Y_2O_3)_{0.01}$ to improve stability of cubic phase

Electrolytes: Ceria

- Ceria based electrolytes work on the same principle as zirconia electrolytes, but usually use another rare-earth element as the dopant (gadolinium, samarium, praseodymium etc.)
  - Doped ceria has much higher ionic conductivity than zirconia (adequate at >450°C)
  - Ceria is an excellent catalyst
  - Most commonly used material is CGO10 ($Ce_{0.9}Gd_{0.1}O_{1.95}$)

  BUT…..
  - Ceria develops electronic conductivity in a reducing atmosphere turning the material into a semiconductor through the formation of polarons
    - Doped ceria doesn't really work as an electrolyte by itself as the cells short out
    - Reduction of Ce^{4+} ions to Ce^{3+} ions with the associated generation of additional oxygen vacancies causes an increase in the lattice parameter of the material which can generate mechanical stresses in the material, potentially large enough to cause the material to crack
- Ceria can be used if combined with a very thin zirconia layer sufficient to block electron transport without adding excessive resistance to ion transport

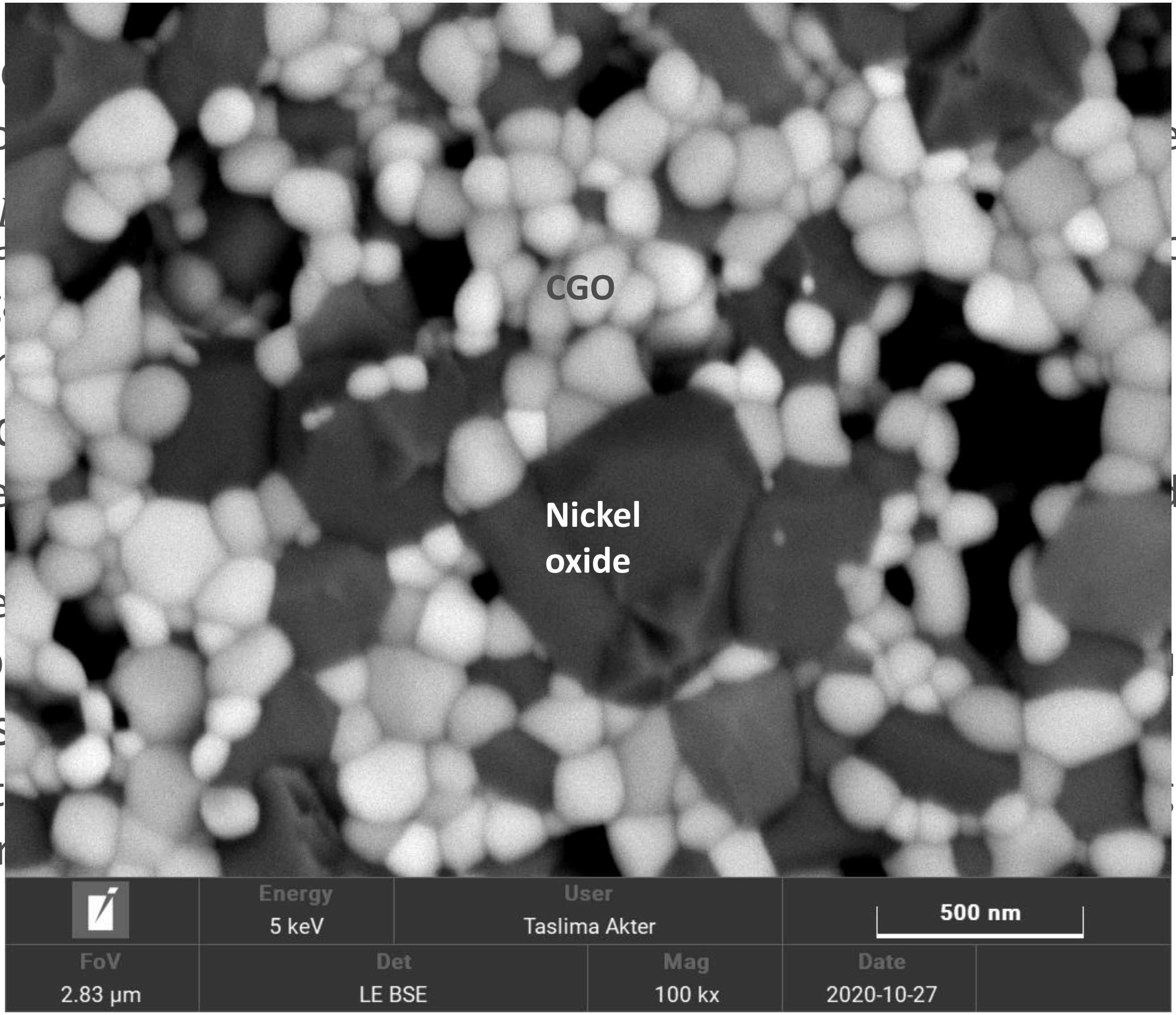
SOC materials: Fuel electrodes

Fuel electrodes

- Primary functions
  - Catalyse the electro… …ctrolysis mode)

$$H_2 + O^{2-} \rightarrow$$

  - Conduct electrons … …onnect
  - Allow diffusion of g…
  - Have a similar therr…
- Most SOC FEs are …
  - Most fuel electrode… …is an excellent catalyst.
  - Most fuel electrode…
  - Fabricated as comp… …on first operation
- Ceramic(oxide) FEs
  - Limited choice of st… …atmosphere
  - Comparatively poor…



SOC Materials: Air electrodes

Air electrodes

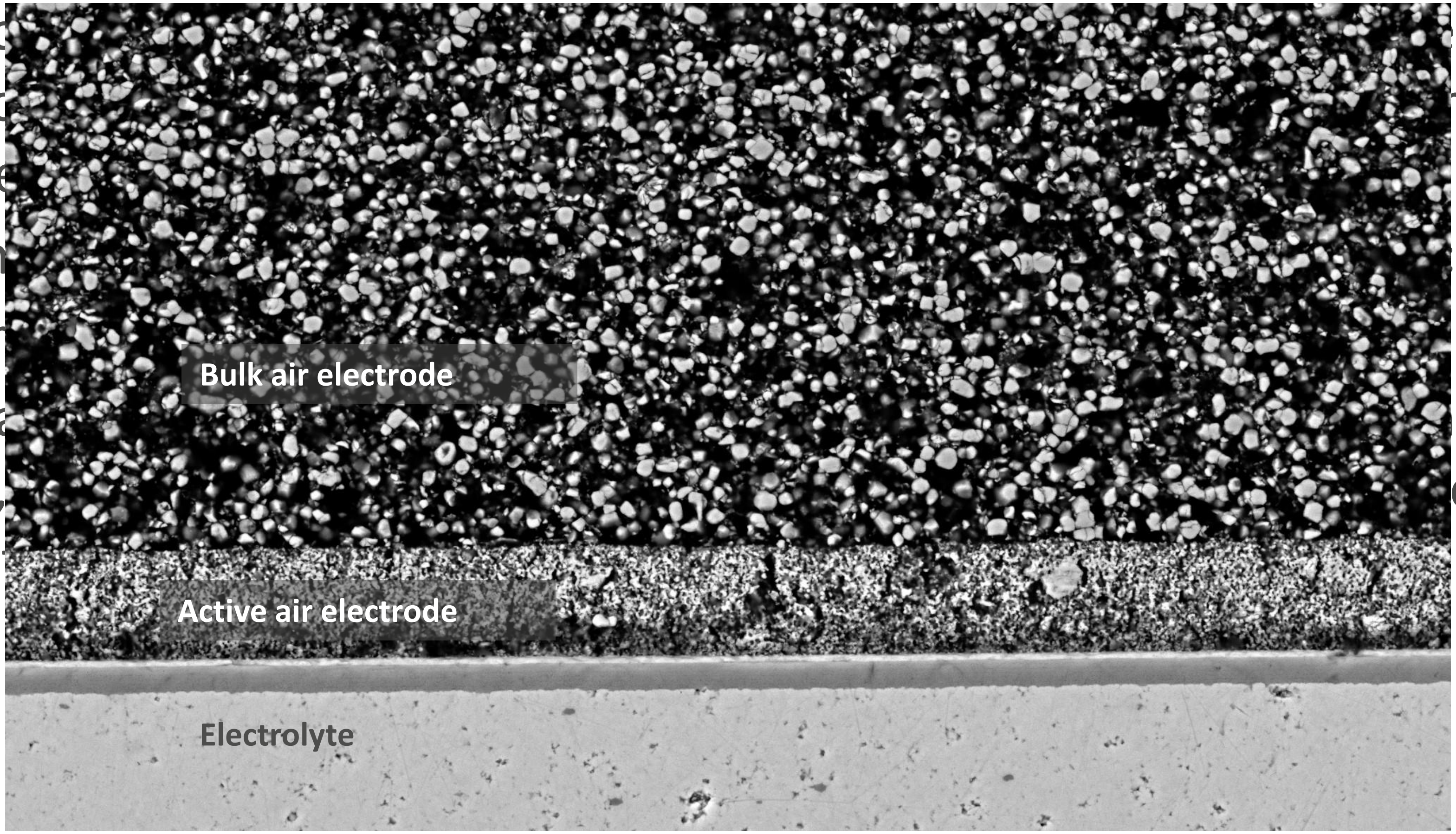
- Primary functions of the air electrode
  - Catalyse the electrochemical reduction of oxygen (or evolution in electrolysis mode)
    $O_2 + 4e^- \rightarrow 2O^{2-}$
  - Conduct electrons away from the cathode-electrolyte interface to the adjacent interconnect
  - Allow diffusion of oxygen to the air electrode electrolyte interface
  - Have a similar thermal expansion coefficient to the electrolyte
- Virtually all SOC air electrodes are electronically conductive ceramics as apart from precious metals most metals are not stable in air at high temperature
  - Most SOCs use air electrodes with the perovskite structure ABO_3
  - A and B are different metal ions (there can be more than one A and B metal ion)
  - Bewildering array of possible air electrode materials
  - Many SOCs use a different material for the catalytically active part of the air electrode and the current collector

Air electrodes: electrocatalysts

- Most widely used electrocatalyst in SOCs is LSCF (typically $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$)
  - Metallic electronic conductor
  - Rapid surface oxygen exchange and oxygen ion conductivity through Co^{3+}/Co^{4+} REDOX couple
  - Iron doping on the B-site reduces thermal expansion coefficient
- LSCF typically used as a composite with CGO which improves electrochemical performance and reduces TEC mismatch with the electrolyte
- LSCF is incompatible with zirconia electrolytes as it forms an $SrZrO_3$ interfacial layer, so a CGO diffusion barrier layer is typically used
- Other perovskites such as LSC ($La_{0.6}Sr_{0.4}CoO_{3-\delta}$) are also used and are more active than LSCF but have a high TEC
- Other material families such as the Ruddlesden-Popper phases such as $Pr_2NiO_{4+\delta}$ have also been shown to be excellent electrocatalysts but not widely adopted due to stability issues

Air electrodes: current collectors

- Current c[…] air electrode to the adjac[…]m the active electrode
- Requiren[…]atalytic activity
- Single-ph[…]
- Other ma[…]um nickelate ($LaNiO_3$),[…]equired to stabilise […]



SOC materials: Interconnects

SOC materials: Interconnects

- Virtually all modern planar SOCs use stainless steel interconnects (ICs)
- Stainless steels are steels containing >12wt% chromium
- Chromium is much more reactive than iron and preferentially oxidises at the surface to form a contiguous, adherent and passivating chromium oxide scale, preventing further oxidation of the material.
- Metals corrode by oxide scale spallation (the oxide scale at the surface is poorly adhered and falls off, exposing fresh metal below to attack); alloying with chromium greatly reduces this tendency.
- Increasing the chromium content improves the oxidation resistance of the steel (to a maximum of 23-25wt%, after which it tends to separate out into a second sigma phase, making the material brittle).
- Stainless steels used for SOC applications are *ferritic* stainless steels (alloys of iron and chromium plus minor elements, and very low carbon content otherwise the steel forms the *martensitic* crystal structure).

SOC materials: Interconnects

- Chromium evaporation is a major issue at SOC operating temperatures on the air side
  - $Cr_2O_3 + 1\frac{1}{2}O_2 + 2H_2O \rightarrow 2CrO_2(OH)_2(g)$
- Chromium poisons air electrodes
- All commercial SOC interconnects are coated on the air side, for example using (MCO) a $Mn_{1.5}Co_{1.5}O_4$ spinel which retains chromium if dense whilst maintaining electronic conductivity

Summary

Summary

- SOCs are a highly efficient technology for both power generation and steam electrolysis
- SOC technology is rapidly approaching commercial maturity driven by a number of industrial developers
- All commercial SOC cells are based on oxygen-ion conducting ceramic oxide electrolytes operating at elevated temperature
- Basic material set for oxygen-ion conducting SOC technology is mature
- Significant scope for materials innovation around
  - Proton conducting electrolytes (still fundamental issues to be overcome)
  - Reduced degradation of SOC materials in service conditions

THANK YOU

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