Imperial College London

SOFC Electrolytes and Anodes

Alan Atkinson Department of Materials Imperial College London SW7 2AZ, UK alan.atkinson@imperial.ac.uk

Aims

- To understand required properties for the electrolytes and anodes
- To understand the properties (and mechanisms underlying the properties) of the most common materials for electrolytes and anodes
- To be aware of problems with the common materials
- To have a broad awareness of research trends and the search for improved materials.

Contents

• Electrolytes

- Requirements for SOFC design and operation
- Point defects (diffusion, ionic and electronic conductivity)
- Common electrolytes
 - Zirconia, ceria, gallates
 - Role of grain boundaries
- Research directions
- Anodes
 - Requirements for anodes
 - Electrode reaction
 - Ionic and electronic conductivity and thermo-mechanical requirements
 - Ni-based anodes
 - Electrochemical performance
 - Fuel reforming and S-tolerance
 - Redox cycling
 - Research directions
 - 3-D microstructures
 - Oxide anodes

Requirements for an electrolyte

- High ionic conductivity (how high?)
- Low electronic conductivity (how low?)
- Stable and constant properties over wide range of oxygen activity and temperature
- Stable over long times (>10,000 h)
- Unreactive towards electrodes and other components
- Good mechanical properties
- "Easy" to process into a leak-free membrane

Review: V.V. Kharton, F.M.B. Marques and A. Atkinson, Solid State Ionics, 174, 2004, 135.

Ionic conductivity

- Metals (and semiconductors) conduct by movement of electrons
- Ionic conductors by movement of ions through the lattice
- Solid oxygen ion conductors by movement of oxygen ions through metal oxide lattice
- Mixed conductors conduct by the movement of oxygen ions and electrons
- Materials are ceramics made up of small crystals fused together by sintering and contain grain boundaries.



Page 6

oxygen ions in the metal oxide lattice

Kröger-Vink notation for point defects

Lattice species	Symbol	Effective charge (electron units)
Metal and oxygen ions on normal sites	M_M^x or O_O^x	Uncharged
Metal interstitial ion	M _i **	2 positive
Oxygen interstitial ion	O _i "	2 negative
Metal vacancy	V _M "	2 negative
Oxygen vacancy	V _O **	2 positive
Higher valency cation (donor)	D _M •	1 positive
Lower valency cation (acceptor)	A _M '	1 negative
Conduction electron	e'	1 negative
Electron hole	h	1 positive

Reactions involving point defects

Rules

- •Maintain electrical neutrality
- Mass balance
- •Stoichiometric site ratio

Doping to create oxygen vacancies $Y_2O_3 \rightarrow (in ZrO_2) 2Y'_{Zr} + \ddot{V}_0 + 3O_0^{\times}$ gives oxygen conductivity

Reduction of a variable valency ion gives n-type semiconduction

 $(CeO_2) \rightarrow \ddot{V}_O + 2e' + \frac{1}{2}O_2$

electron can be regarded as temporary Ce³⁺ ion

Defect equilibrium calculations

Defect reaction
$$(\text{CeO}_2) \rightarrow \ddot{\text{V}}_0 + 2e' + \frac{1}{2}\text{O}_2$$

Electrical neutrality (undoped) $2[\ddot{\text{V}}_0] = n$
Electrical neutrality (Gd-doped) $2[\ddot{\text{V}}_0] = n + [\text{Gd}'_{\text{Ce}}]$

Equilibrium constant
$$\begin{bmatrix} \ddot{V}_0 \end{bmatrix} n^2 P_{O2}^{\frac{1}{2}} = K$$

$$n \propto P_{\text{O2}}^{-\frac{1}{4}}$$
 (doped) or $n \propto P_{\text{O2}}^{-\frac{1}{6}}$ (undoped)

Oxidation, reduction and electronic conductivity

Electrons and holes have higher mobilities than ions Variable valence metal ions (e.g. transition metals) are bad for solid oxide electrolytes



Log P_{O2}

Log P_{O2}

Ionic transference number

$$t_{ion} = \frac{\sigma_{ion}}{\sigma_{ion} + \sigma_{el}}$$

For a SOFC electrolyte working over a range of P_{O2}

$$\langle t_{ion} \rangle = \frac{\int_{anode} d(\ln(P_{O2}))}{\ln(P_{O2}^{cathode}) - \ln(P_{O2}^{anode})}$$

Need $< t_{ion} >$ to be close to 1 e.g.>0.99

Ionic Conductivity

$$\sigma = N \frac{q^2}{kT} \gamma \left[\ddot{\mathbf{V}}_{\mathrm{O}} \right] \left(1 - \left[\ddot{\mathbf{V}}_{\mathrm{O}} \right] \right) a_0^2 v_0 \exp \left\{ \frac{-\Delta H_m}{kT} \right\}$$

Equation for conductivity contains concentration of vacancies plus a term which indicates how easily they move through the crystal lattice.



 ΔH_m is "migration enthalpy"

lons jump from site to siteRequires a vacant site to jump into

•Jumps biased by electric field

•Jumps require thermal energy to get over energy barrier.

•Need low ΔH_m for high ionic conductivity

Ionic Conductors for SOFC

•Arrhenius plot is convenient for comparing electrolytes •Strictly should plot $\sigma T vs 1/T$ but easier to understand plot of $\sigma vs 1/T$ •Aqueous 1M NaCl solution has conductivity of 0.1 S cm⁻¹ at 25°C





 $ASR = (V_0 - V)/I = 0.3 \text{ ohm } \text{cm}^2$

Maximum tolerable from a single source = 0.15 ohm cm² Single cell data do not usually include interconnection losses

Practical constraints for SOFC electrolyte selection



B. Steele, Phil. Trans. R. Soc. London A (1996)

Fluorite structure materials

- Based on metal oxides with the formula MO₂ (M⁴⁺)
- "Doped" with oxides with lower metal ion charge (usually M³⁺) e.g. Y₂O₃
- Simple cubic structure.
- Leads to materials with very high conductivities
- Two common Materials are;
 - $Zr_{1-x}Y_{x}O_{2-\delta}$ (YSZ)
 - $Ce_{1-x}Gd_xO_{2-\delta}$ (CGO)



ZrO₂ needs to be stabilised in cubic form

Cubic needs 9 mol % Y₂O₃

Or 18 mol % YO_{1.5}



Which is best trivalent dopant for zirconia?



- Y is most commonly used
 Sc gives higher conductivity,but is more expensive.
- •Important criterion is that dopant should have similar size to Zr⁴⁺

• 96.5 kJ mol⁻¹ = 1 eV atom⁻¹

Arachi et al, Solid State Ionics 121 (1999) 133

How much dopant to add?



Arachi et al, Solid State Ionics (1999)

•Adding more trivalent dopant eventually is counter productive

•Oxygen vacancies and dopant ions have opposite effective charge

•They attract each other and form immobile defect clusters at high concentrations

•Hence 8YSZ is popular

Sc-doped zirconia



Politova and Irvine, Solid State Ionics 168 (2004) 153

Double-doped ScSZ



Alternatives to zirconia

- Doped ceria
- Doped LaGaO₃
- Other perovskites (LnBO₃)
- BIMEVOX
- LAMOX $(La_2Mo_2O_9)$
- Ba₂In₂O₅ (Brownmillerite structure)
- Pyrochlores (Gd₂Zr₂O₇)
- Apatites

Dopant selection for CeO₂



Page 23 Kharton et al, J. Mat. Sci. (2001)

Electronic conductivity in CGO



•n-type electronic conduction dominant in SOFC fuel environment above 570°C •Caused by $Ce^{4+} \rightarrow Ce^{3+}$

•Also expands lattice leading to mechanical problems

Effect of CGO reduction on SOFC performance



- •Lowers efficiency at low power
- •Smaller effect on efficiency at typical cell voltage (0.7V)
- Gets worse as temperature increases or electrolyte thickness decreases
 Max operating T for doped ceria is 600°C
- •Can use a thin layer of ScSZ to block electronic conduction (bi-layer electrolyte) Page 25



Perovskite LSGM electrolytes





2



Perovskite crystal structure

Apatite structures RE_{9.33+x}(Si,GeO₄)₆O_{2+3x/2}



Oxygen "interstitial" diffusion along channels



Kendrick, et al. Chem. Commun., 2008, 715

 $La_{1.54}Sr_{0.46}Ga_{3}O_{7.27}$ (melilite)





X. Kuang et al., Nature Materials 7 (2008) 498

Proton-conducting oxides



$$H_2O + \ddot{V}_O + O_O^{\times} \rightarrow 2O\dot{H}_O$$

•Protons incorporated from water vapour

•Tend to be expelled at high temperatures

Kreuer, Ann. Rev. Mat. Res. (2003)

BaZr _{0.7}Pr _{0.1}Υ _{0.2}O _{3-δ}



Conductivity complex mixture of protons, oxygen vacancies and electron holes
 Claimed to be more stable than BCY in CO₂ and
 Lower grain boundary resistance than BZY

SOFC electrolytes are polycrystalline ceramics





Grain boundaries act as extra series resistance to the crystal grains

AC Impedance Technique



Components of the conductivity can be separated by measuring ac impedance

Component due to grains (bulk)

Component due to grain boundaries

Model space charge in 8YSZ at 500°C

X. Guo and J. Maier, J. Electrochem. Soc., **148** (2001) E121.



Even "clean" grain boundaries are resistive compared with lattice

Diffusion/conductivity in nanocrystalline YSZ

Diffusion along GBs 1000x faster than in lattice?

Not supported by more recent work



G. Knoner et al., Proc. Nat. Acad. Sc. USA, 2003

N.H. Perry et al., J Mater Sci (2008) 43:4684-4692

Grain boundaries always reduce total conductivity of fast ion conductors

"Colossal" ionic conductivity of thin YSZ/SrTiO₃ films?



Enhanced conduction along the YSZ/SrTiO₃ interface

lonic or electronic?

Not been repeated

Strain and space charge effects at interfaces still not resolved

. Garcia-Barriocanal, et al. Science 321, 676 (2008); Science 321, 676 (2008); Science 321, 676 (2008);

Summary for electrolytes

- Target conductivity is 0.01 S cm⁻¹
- YSZ most popular
- ScSZ better for lower temperatures (> 600 °C)
- Ceria (Gd or Sm doped) good for lower T (500 600°C)
 Needs electronic blocking layer
- LSGM popular in Japan
- Other contenders so far do not offer sufficient advantage
 Have we reached a limit?
- Grain boundaries are an important source of extra resistance
 - Must keep them clean
 - Nano crystalline electrolytes have no advantage
- Sr and Ba zirconates and cerates are viable proton conducting electrolytes

Thank you for your attention!

Questions on electrolytes?

Requirements for electrodes

Essential

- High ionic conductivity (how high?)
- High electronic conductivity (how high?)
- Electrocatalytic for electrode reaction (high concentration of active sites)
- Porous for gas access
- Stable over long times (>10,000 h) in fuel conditions
- Unreactive towards electrolyte and other components
- Easy to fabricate

•Desirable

- -Good thermo-mechanical properties (especially when also used as cell support)
- -Tolerant of vapour-borne impurities (e.g. S for anodes or Cr for cathodes)
- -Anodes should be able to cycle between reducing and oxidising conditions

Reviews for anodes: A. Atkinson et al., Nature Materials 3 (2004) 17 W.Z. Zhu and S.C. Deevi, Materials Science and Engineering A, 362 (2003)228. Page 38

Triple phase boundary electrodes (Ni/YSZ cermet)



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

•Both ionic and electronic components must percolate (and pores) Page 39 •Microstructure is important

Electrocatalyst (Ni) has high electronic conductivity, but low ionic conductivity

Reaction site is "at" triple phase boundary (gas-electrocatalyst-electrolyte) or TPB

Composites with a good ionic conductor (e.g. the electrolyte) often used to improve performance



Theory for porous single phase electrode (or fine structured composite)

Adler, Lane, and Steele, J. Electrochem. Soc., 143 (1996) 3554



More detail when we look at cathodes

Effective thickness of anode



H. Fukunaga et al., ECS Transactions, 7 (1) 1527-1531 (2007)

Typically only approx. 20 μ m is active for high performance anode

Electrochemical kinetics



Overpotential of the electrode, η, is difference between actual electrode potential (current flowing) and equilibrium electrode potential (zero net current or open circuit)

If overpotential causes the oxidation reaction to proceed $(\eta \text{ positive})$ it is anodic

If overpotential causes the oxidation reaction to reverse (η negative) it is cathodic

Polarisation resistance (ohm cm²), $R_p = \frac{\eta}{i}$

Typical polarisation curves for Ni/YSZ at 850°C C.J. Wen, et al., J. Electrochem. Page 42 Soc. 147 (2000) 2076

Electrochemical kinetics 3-electrode measurement



Can also impose small AC signal to carry out impedance spectroscopy to try and look at different contributions.

Reference electrode position needs care.

$$\begin{split} \eta = \eta_{activation} + \eta_{concentration} + \eta_{ohmic} \\ & \text{Butler-Volmer} \quad & \text{Gas diffusion} \quad & \text{Current collection} \end{split}$$

Electronic conductivity required for current collection

Depends on cell design for resistance target < 0.1 ohm cm²



Thermo-mechanical requirements

Depends on cell design

Thin layers are constrained by the stiffest layer in the structure



Delamination: thin layer in compression

Cracking: thin layer in tension





For stability need: tough material, low elastic modulus, thin layers, low CTE mismatch

Ni/YSZ anodes and anode supports

•Ni/YSZ cermet is not a single material, but a whole family

•Made by sintering a mixture of NiO and YSZ and then reducing NiO to Ni when cell is first operated



Page ⁴⁶S.K. Pratihar et al., SOFC-VI (1999) 513.

Properties depend on:

- •Content of NiO and YSZ
- •Particle sizes of NiO and YSZ
- •Porosity (often increased by pore-formers)
- •Sintering temperature
- Interconnected networks of Ni and YSZ must both percolate
- •CTE approx 12.5-13 ppm/K



Ni/YSZ microstructure by FIB tomography





TPBs

Electrochemical model of tomographic TPB



"model" exchange currents (+) are from patterned Ni electrodes

P. Shearing et al., Journal of Power Sources, 195 (2010) 4804

More detailed models of Ni/YSZ



S. Gewies and W.G. Bessler, J. Electrochem. Soc. 155 (2008) B937.

Comparison with experiments



Low frequency arc due to transport in gas channels

Mid frequency arc due to gas transport in cermet pores

High frequency arc due to electrochemical reaction

Hydrocarbon fuels

Electrochemical reactions?

 $\mathrm{CH}_{4} + 4\mathrm{O}^{2\text{-}} \rightarrow \mathrm{CO}_{2} + 2\mathrm{H}_{2}\mathrm{O} + 8\mathrm{e}^{\text{-}}$

 $\mathrm{CO} + \mathrm{O}^{2\text{-}} \rightarrow \mathrm{CO}_2 + 2\mathrm{e}^{\text{-}}$

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

Only significant electrochemical reaction ?

Chemical reactions

- $CH_4 \rightarrow C + 2H_2$
- $CH_4 + H_2O \rightarrow CO + 3H_2$
- $\mathrm{CH_4} + \mathrm{CO_2} \rightarrow \mathrm{2CO} + \mathrm{2H_2}$

 $CO + H_2O \leftrightarrow CO_2 + 2H_2$

 $2CO \rightarrow C + CO_2$

Carbon deposition

Steam reforming

Shift reaction Boudouard reaction

Ni promotes C deposition therefore needs H_2O/CH_4 > 2



Anode redox problems: Ni-based cermets



Ni cermet redox dimensional changes



Microstructural design of Ni/YSZ for redox tolerance



M. Pihlatie et al, J. Power Sources 193 (2009) 322

Poisoning by sulphur



Reversible poisoning at low S concentrations NiS formation at higher concentrations Worse at lower temperatures (need S < 0.1 ppm at 750°C)

Y. Matsuzaki and I. Yasuda, Solid State Ionics 132 (2000) 261

Defects in transition metal perovskites e.g. La_{1-x}Sr_xMO₃

Acceptor doping $2SrO \rightarrow 2Sr'_{La} + 2O^{\times}_{O} + V^{\bullet}_{O}$ Reduction $O^{\times}_{O} \rightarrow V^{\bullet\bullet}_{O} + 2e^{-} + \frac{1}{2}O_{2}(g)$ Electronic $null \rightarrow e' + h^{\bullet}$ M valency changeSchottky $null \rightarrow V^{\prime\prime\prime}_{La} + V^{\prime\prime\prime}_{M} + 3V^{\bullet\bullet}_{O}$



in this range in anode conditions gives low electronic conductivity



$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3 \text{ p-type oxide anode}$



Redox tolerant Resistant to C deposition

S.W. Tao and J.T.S. Irvine, Nature Materials 2 (2003).

Current collection problem (low electronic conductivity)



Page 57

Doped SrTiO₃ n-type oxide anodes



n-doped SrTiO₃ anodes



Ruiz-Morales et al., Nature (2006)

Current collection problem (low electronic conductivity)

YSZ impregnated with Cu and CeO₂



R.J. Gorte et al., Adv. Mater. 12 (2000) 1465

Current research directions for anodes

- Durability
 - Ni coarsening
- Lower temperatures
 - High surface areas by impregnation
 - Composites with lower temperature electrolytes
- S and C tolerance
- Redox tolerance
 - Lower Ni content microstructures
 - Stiff YSZ frameworks
 - Oxide anodes
- Mechanisms and modelling

Thank you for your attention!

Questions on anodes?