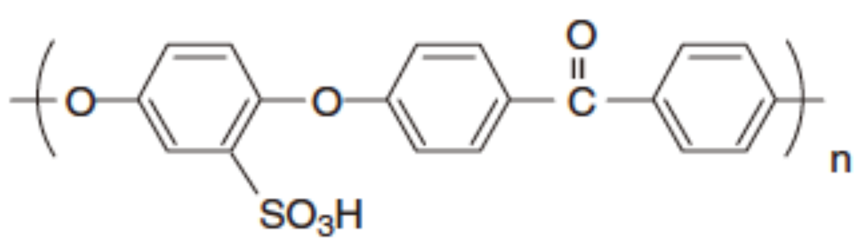
Fuel Cell Materials

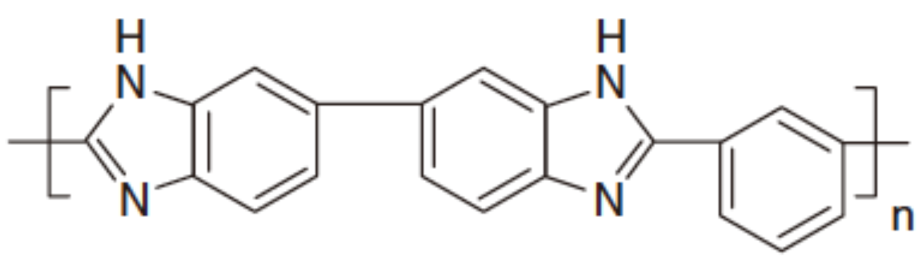
PEMFC Electrolyte

- Perfluorinated Polymers (e.g., Nafion)
- Sulfonated Hydrocarbon Polymers (e.g., Polyeth eretherketone = PEEK)
  - Diverse and less expensive
  - Improve high-temperature hydration
  - Easy recycling
  - Less stable
  - Lower ionic conducrivity



PEMFC Electrolyte

- Phosphoric Acid Doped Polybenzimidazole (PBI)
  - Doped with with a strong acid (H_3PO_4)
  - No liquid water required
  - Stable up to 200C
  - Free-acid vehicle mechanism
  - 100 times less expensive than Nafion
  - Durability issues related to acid leaching, membrane oxidation, slow cathode kinetics under phosphoric acid
  - Pt/C ink formulation



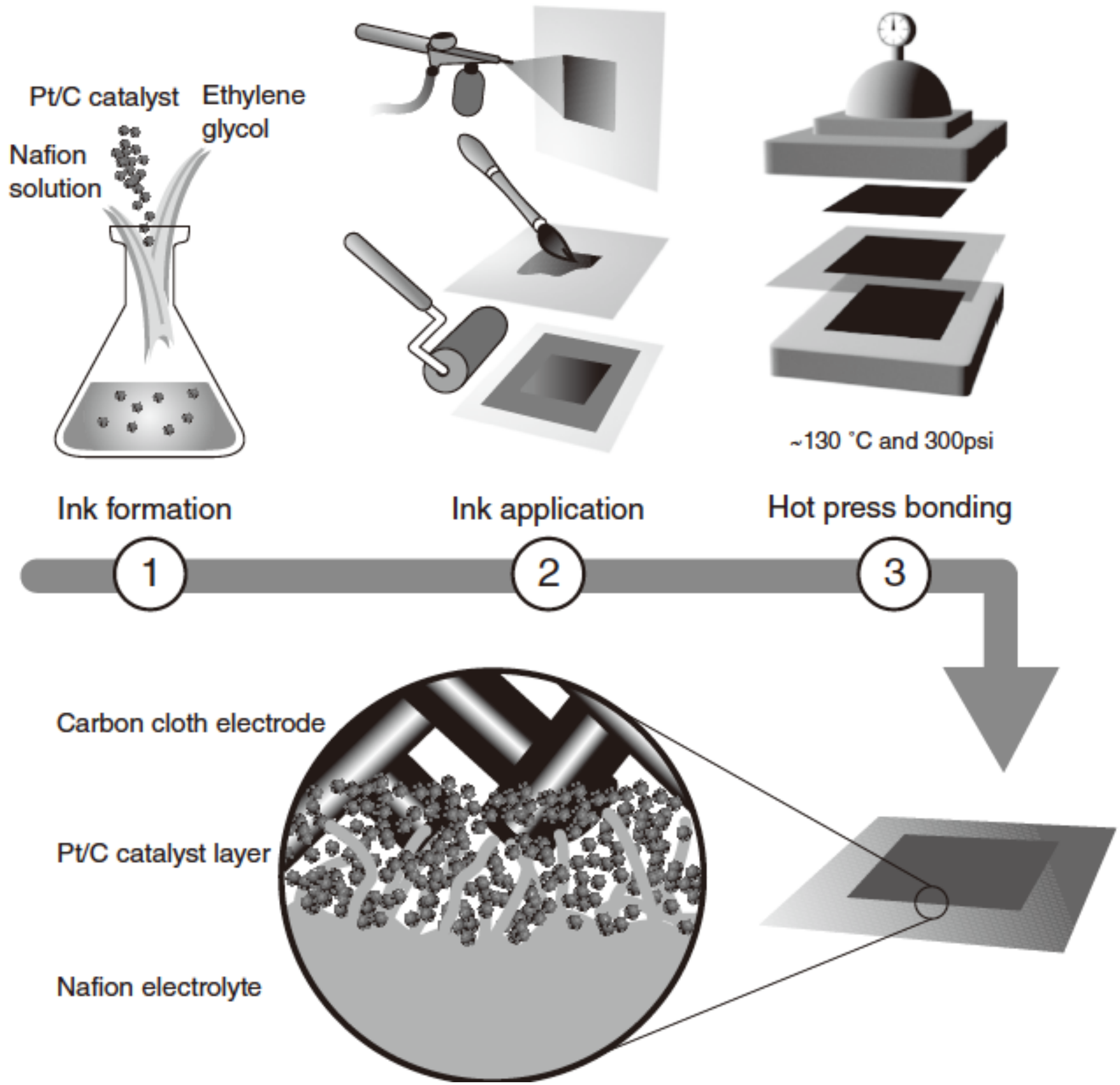
PEMFC Electrolyte

- Polymer–Inorganic Composite Membranes
  - Nanoparticles/microparticles in Nafion
  - Water retention by hydroscopic oxide (e.g., SiO_2 or TiO_2)
  - Proton-conducting materials such as phosphates (e.g., zirconiu m phosphates) and heteropolyacids (e.g., phosphotungstic acid and silicotungstic acid)
  - Operation over 100C
  - Still need humidification
  - Low conductivity
  - Weak mechanical integrity

PEMFC Electrolyte

- Solid-Acid Membranes
  - H_2SO_4, H_3PO_4, K_2SO_4 -> $CsHSO_4$,CsH_2PO_4
  - Phase transition for rotational diffusion transfer mechanism (>10^{-2} S·cm)
  - Operation at 100C~200C
  - Poor mechanical properties and ductility
  - Water solubility
  - Thermal expansion

PEMFC ELECTRODE/CATALYST MATERIALS



Catalyst

- Nanoscale (2–3 nm) metal particles (electroless plating)
- High-surface-area carbon powder support (such Vulcan X C-72)High catalytic activity
- High surface area/high density of triple-phase boundaries
- Percolating electrical and ionic conductivity
- High stability/corrosion resistance
- Excellent poison/impurity tolerance
- Minimal degradation
- Low cost (if possible!)

Anode Catalyst

- Pt/C catalyst
  - ultrasmall (2–3 nm) Pt particles on carbon powder
  - 0.05 mg Pt/cm^2
  - 50 kW fuel cell stack: 2.5 g of Pt at the anode ~ $100
  - Platinum Alloys (for Direct Alcohol Fuel Cells)
- Pt alloy
  - Alcohol oxidation
  - CO poisoning on Pt
  - Methanol oxidation: Ru(best), Sn, W, or Re.
  - Ru generates OH_{ads} to oxidize CO
  - PtRu + W or Mo for methanol
  - Pt–Sn alloys for ethanol: very slow kinetics

Cathode Catalyst

- Pt/C catalyst
  - ultrasmall (2–3 nm) Pt particles on carbon powder
  - Request at least 0.4 mg Pt/cm^2
  - Too small particle reduce activity
    - Oh_{ads} inhibition

- Pt alloy
  - 25~75% Pt in Pt–Ni, Pt–Cr, Pt–Co, Pt–Mn, Pt–Fe, Pt–Ti
  - Pt_3Cr, Pt_3Co: 2–4 times ORR enhancement
  - Harder to deploy as small particle on carbon supports
  - Leached-out Co, Cr, Fe, Ni, Ti poison the PEMFC
  - Leaching-out, accelerated degradation, corrosion, and deactivat ion.

Cathode Catalyst

- Non-platinum ORR Catalysts
  - Volumetric catalytic activity: > 1/10 of Pt
  - 10 times more loading (limitation on catalyst layer volume)
  - No non-noble metal satisfies the requirments
- Metal Macrocycles
  - Transition metal ion(Fe or Co) stabilized by several nitrogen ato ms (aromatic or graphite like carbon structure)
  - Similar to active center of hemoglobin
  - Polymerized iron phthalocyanine, cobalt methoxytetraphenylpor phyrin
- Doped Carbon
  - High-surface-area carbon materials, doped with Fe, N, B
  - Best ORR activities of any of the non-Pt catalyst

Gas Diffusion Layer

- Carbon Cloth: weaved carbon fiber filaments
  - Mechanical resilient
  - Low density (~0.3 g⁄cm3)
  - High permeability (~50 Darcys)
  - 350–500 μm thick
  - Compress significantly (30–50%) when clamped
- Carbon Paper: carbon fibers in paperlike sheet
  - Binder (carbonized resin) for mechanical integrity
  - Denser (~0.45 g⁄cm3) and less permeable (~10 Darcys)
  - Stiff and somewhat brittle
  - 150–250 mm thick
  - Less compression (10–20%)

Gas Diffusion Layer

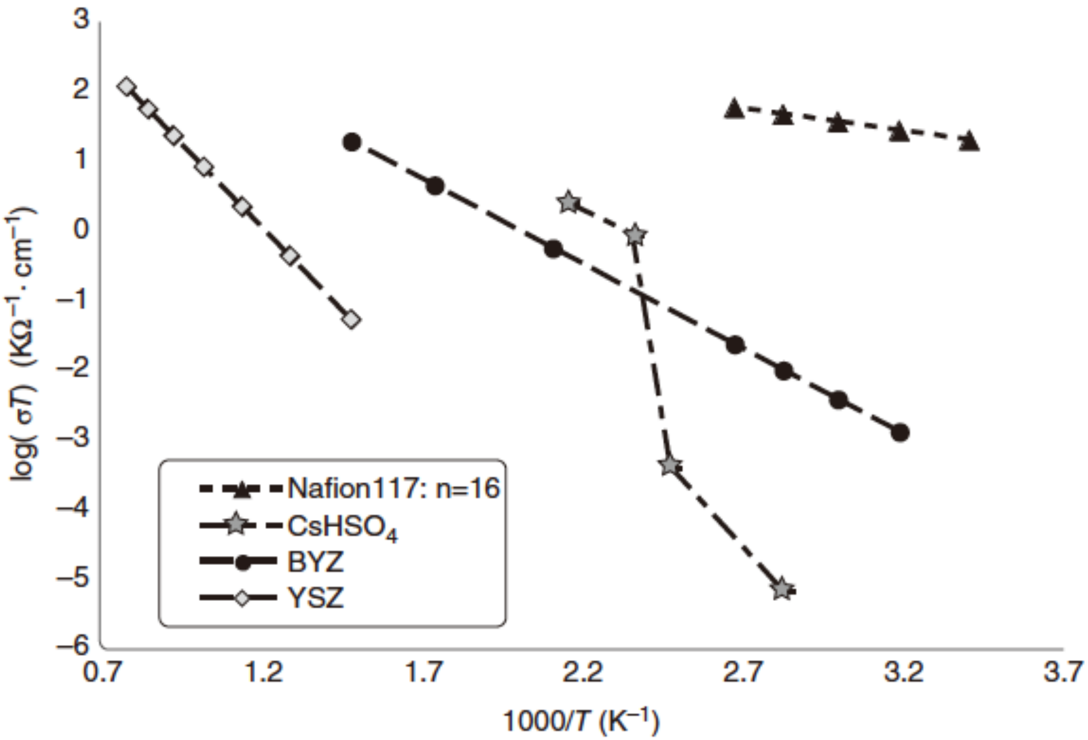
- Hydrophobic Treatment: prevent flooding
  - PTFE treatment (5 ~ 30% wt loading)
  - Dipping into an aqueous PTFE suspension / baking at 350–400 ∘C
- Microporous Layers
  - Transition from GDL(10–30μm pores) to catalyst(10–100nm pores)
  - Improve the wicking of liquid water from the catalyst layer
  - Decrease the electrical contact resistance between the GDL and the catalyst layer.
  - Submicrometer-sized particles of graphite with PTFE
  - Thin, uniform, microporous graphitic layer ∼20–50 μm thick
  - Seven-layer MEA or "Electrode Los-Alamos Type" (ELAT) (anode GDL, anode microporous layer, anode catalyst layer, electrolyte, cathode catalyst layer, cathode microporous layer, cathode GDL.)

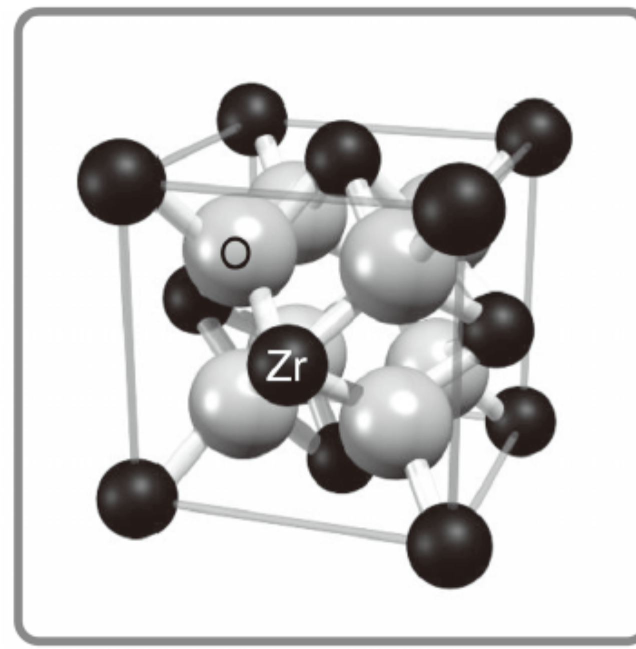
Gas Diffusion Layer Requirements

- High electrical conductivity
- High gas permeability
- High stability/corrosion resistance
- Facilitation of water removal
- Good mechanical properties
- Low cost

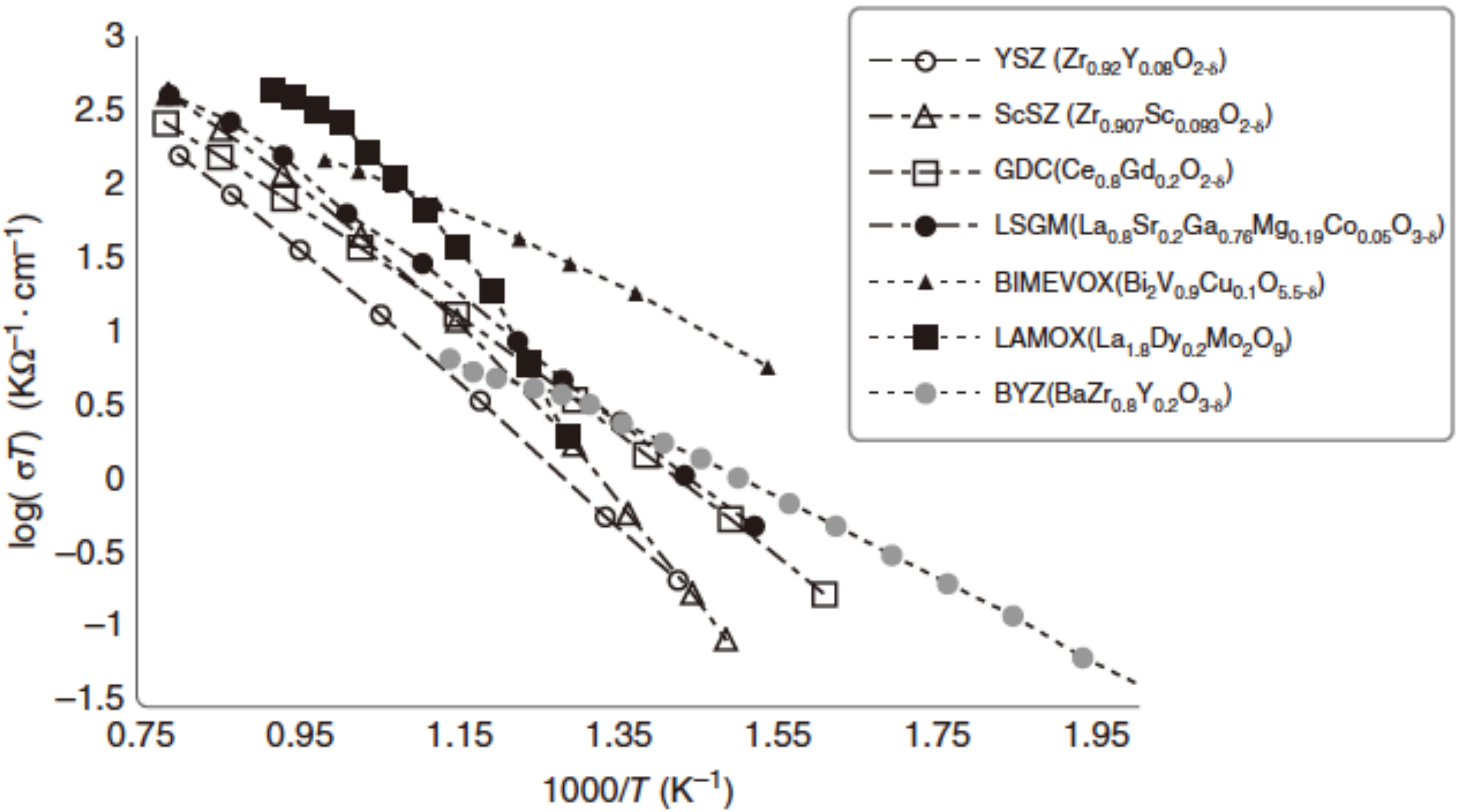
SOFC Electrolyte

- Yttria-Stabilized Zirconia
  - 6–8% molar Y_2O_3 in ZrO_2



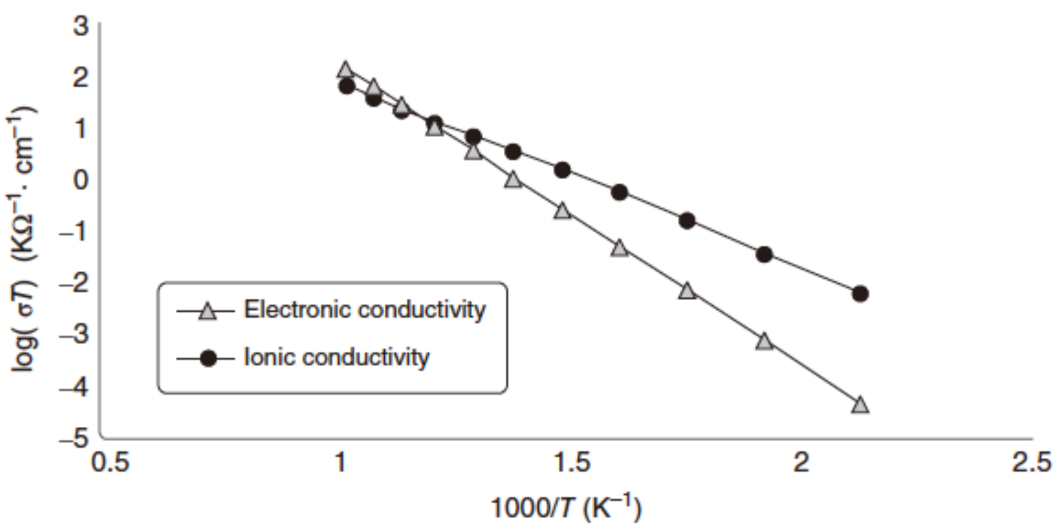


SOFC Electrolyte



SOFC Electrolyte

- Doped Ceria
  - GDC10(CGO10): $Ce_{0.9}Gd_{0.1}O_{1.95}$
  - High conductivity : 0.01 S·cm^{-1} at 500 ∘ C
  - Fluorite structure like YSZ
  - Reduction of Ce^{4+} to Ce^{3+} in hydrogen
    - n-type electronic conductivity
    - Mechanical failure due to expansion

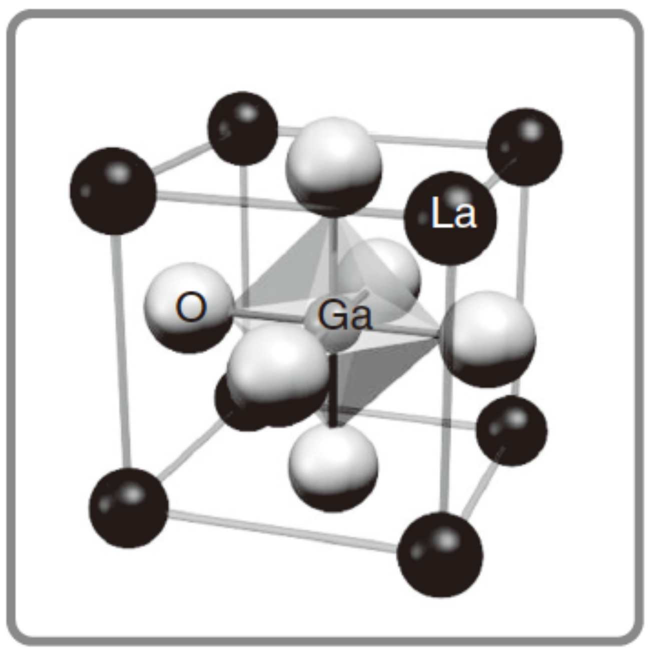


SOFC Electrolyte

- Bismuth Oxides
  - α-Bi_2O_3(monoclinic at RT), δ-Bi_2O_3,(cubic-fluorite at 727∘C)
  - Very high conductivity (~1 $S \cdot cm^{-1}$ at 750 ∘ C)
  - Intrinsically “defective” fluorite-type crystal structure
  - Very high (25%) oxygen vacancy
  - Stabilized δ-Bi_2O_3 with Y, Dy, Er for low T
  - BIMEVOX
    - γ -$Bi_4V_2O_{11}$
    - $Bi_2V_{1-x}Cu_xO_{5.5-\delta}$, $Bi_2V_{1-x}Ni_xO_{5.5-\delta}$
    - High chemical reactivity and low mechanical strength
- LAMOX($La_2Mo_2O_9$)
  - $La_{1.7}Bi_{0.3}Mo_2O_{9-\delta}$, $La_2Mo_{1.7}W_{0.3}O_{9-\delta}$, $La_2Mo_{1.95}V_{0.05}O_{9-\delta}$

SOFC Electrolyte

- Perovskite Oxides
  - $LaGaO_3$: $La_{0.9}$ $Sr_{0.1}$ $Ga_{0.8}$ $Mg_{0.2}$ $O_{3-\delta}$
  - Less reducible
  - Volatilization of gallium
  - Undesirable secondary phases
  - Reactivity with cathode electrode materials



SOFC Electrolyte

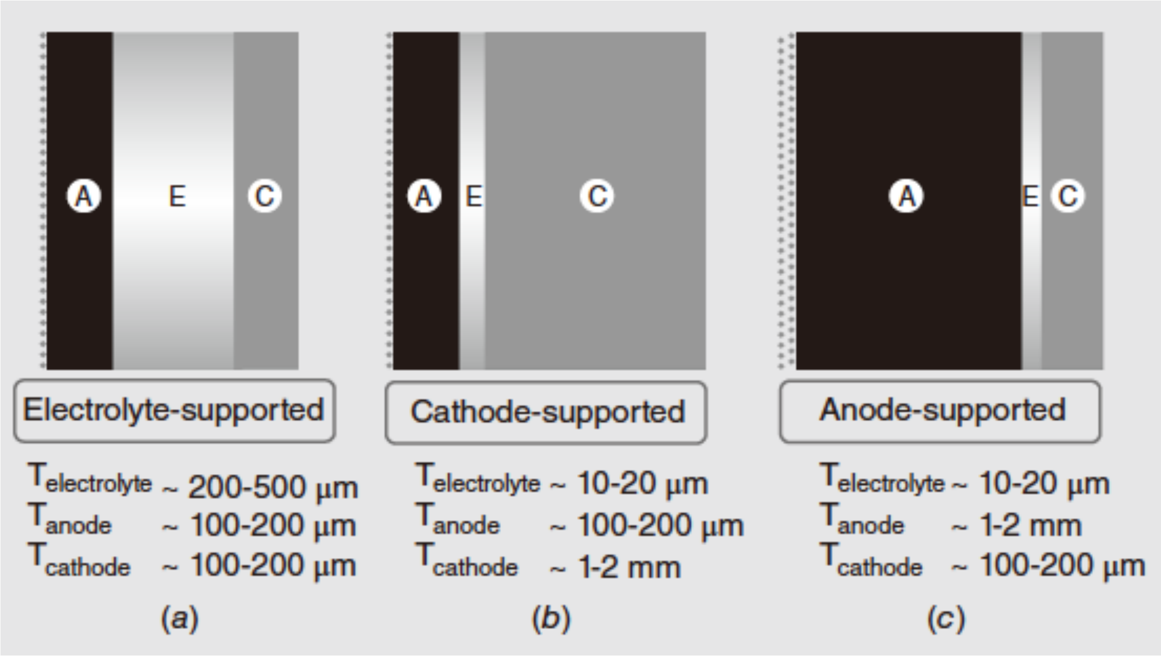
- Perovskite Oxides
  - $BaZrO_3$
    - Very high proton conductivity
    - 0.1 $S \cdot cm^{-1}$ at 500∘C
    - Yttrium-doped barium zirconate (Y:$BaZrO_3$ or BZY)

SOFC Electrode

- High catalytic activity
- High electrical conductivity
- Thermal/chemical stability
- High-temperature compatibility with the SOFC el ectrolyte and interconnect material
  - Thermal expansion matching, limited reactivity
- Durability at high temperatures
- Fuel flexibility/impurity tolerance
- Coking resistance desired
- Low cost

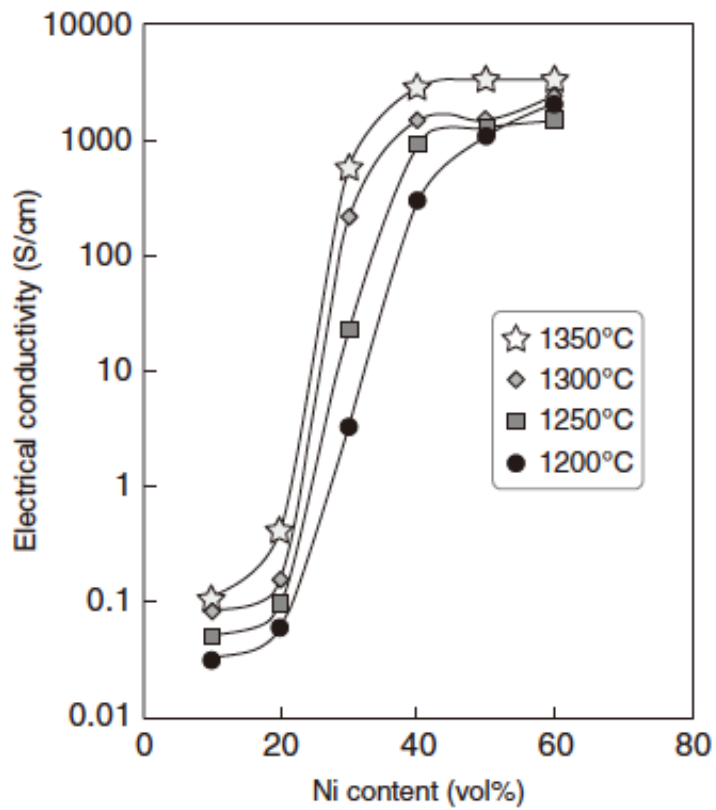
SOFC Electrode

- Dual layer
  - Catalytically active functional layer
    - 10–30 μm thick
    - high density of TPB
  - Mechanical support laye
    - 100 μm–2 mm thick,
    - Protection for the catalyst layer



Ni–YSZ Cermet Anode

- Thermal expansion match with electrolyte
- Degradation
  - Ni coarsening, agglomeration, or oxidation
  - Carbon coking



SOFC Anode

- Ceria-Based Anode
  - Good electrocatalyst for methane oxidation
  - GDC40 for dimensional stability
  - Ni, Co, Pt, Rh, Pd, Ru for activity enhancement
- Perovskite Anode Materials
  - $La_{0.8}Sr_{0.2}Cr_{0.97}V_{0.03}O_3$
  - LSCV–YSZ

SOFC Cathode

- Strontium-doped $LaMnO_3$
  - Good physical and chemical stability
  - High electrical conductivity and catalytic activity
  - Low oxygen conductivity
  - LSM–YSZ composite

- LSCF($La_{1-x}Sr_xCo_{1-y}Fe_yO_3$)
  - High oxygen conductivity
  - Fe prevents $LaCoO_3$ reaction with YSZ

- $Sm_{0.5}Sr_{0.5}CoO_3$

SOFC Interconnect Materials

- High electronic conductivity
- Thermal expansion match
- Good thermal conductivity
- Non-reactivity
- Low permeability
- Dimensional, chemical stability
- Good strength and creep resistance
- Resistance to sulfur and carbon poisoning and r esistance to oxidation
- Ease of fabrication; low cost

SOFC Interconnect Materials

- Ceramic Interconnects
  - Ca-doped $LaCrO_3$
    - High electrical conductivity
    - Ionic conductivity
  - Mg- and Sr-doped $LaCrO_3$
    - Less oxygen permeation
    - Poor air sinterability

- Metal Interconnects
  - $94Cr–5Fe–1Y_2O_3$
  - CrO_3 or $CrO_2(OH)_2$ poisoning