Preparation and characterization of anode catalysts for the direct alcohol fuel cells (DAFC): methanol and ethanol

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Introduction

• To reduce pollution produced by burning fossil fuels, energy production must become cleaner and the use of energy more effective.

• Alternatives to fossil fuel: Wind power, Solar PV, Fuel cell (FC)…

• FC offer an attractive combination of highly efficient fuel utilisation and environmentally-friendly operation

• Device that uses a chemical fuel such as hydrogen and an oxidant, e.g., oxygen to generate electricity directly from electrochemical processes

• The by-products from an operating fuel cell are heat and water
Types of fuel cells (FC)

- **Alkaline Fuel Cell (AFC):** Electrolyte-alkaline potassium hydroxide, 80°C
- **Molten Carbonate Fuel Cell (MCFC):** Electrolyte-carbonate-salt-impregnated ceramic matrix, 650°C
- **Solid Oxide Fuel Cell (SOFC):** Electrolyte- hard, non-porous ceramic compound, 700-1000°C
- **Phosphoric Acid Fuel Cell (PAFC):** Electrolyte-liquid phosphoric acid, 180-200°C
- **Polymer Electrolyte Membrane Fuel Cell (PEMFC):** Electrolyte- solid polymer membrane (typically Nafion), around 70°C

Besides H₂ as fuel, chemical energy in alcohols can be directly converted into electricity. Examples: methanol and ethanol
WHY DAFC?

- Easy transportation and storage of the fuel
- Does not require a reformer
- Liquid fuel is compatible to existing infrastructure
- High energy density (ethanol 8kWh/kg, methanol 6.1kWh/kg)
Challenges of DAFC

- Alcohol crossover from anode to cathode catalyst.
  ORR catalyst tolerant to alcohol,
  membrane reduce alcohol crossover
- CO poisoning on anode catalyst
- Catalyst able to break C-C bond

DEFC vs DMFC

- Ethanol: low toxicity and widely available but its reactivity is slightly lower than methanol’ reactivity.
Electro-catalysts

• Best binary catalysts for methanol and ethanol electro-oxidation: Pt-Ru and Pt-Sn respectively.

• The enhanced performance is not good enough in the presence of CO.

• More active electro-catalysts are critically needed

• Ternary catalysts: Iridium may promote the oxidation of the adsorbed CO on Pt.

• Non-metallic elements (N, P and S), reduces the size of a PtRu/C catalyst
Preparation of Electro-catalysts

Method 3

Reducing agents: Formic acid and NaH$_2$PO$_2$.H$_2$O

$$\text{PtCl}_6^{2-} + 2\text{H}_2\text{PO}_2^- + 2\text{H}_2\text{O} = 2\text{H}_2\text{PO}_3^- + 4\text{H}^+ + 6\text{Cl}^- + \text{Pt}$$

$$\text{IrCl}_6^{2-} + 2\text{H}_2\text{PO}_2^- + 2\text{H}_2\text{O} = 2\text{H}_2\text{PO}_3^- + 4\text{H}^+ + 6\text{Cl}^- + \text{Ir}$$

$$\text{Sn}^{2+} + \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} = \text{H}_2\text{PO}_3^- + 2\text{H}^+ + \text{Sn}$$

$$6\text{H}_2\text{PO}_2^- = 2\text{H}_2\text{PO}_3^- + 2\text{H}_2\text{O} + 4\text{OH}^- + 4\text{P}$$

$$2\text{H}_2\text{PO}_2^- + 2\text{H}_2\text{O} = 2\text{H}_2\text{PO}_3^- + 2\text{H}_2$$

Molar ratios
Pt:Sn:Ir (3:1:1)
Pt:Ru:Ir (3:3:1)

Total catalyst loading: 20wt%
Experimental set-up: Electrochemical Characterization

Potentiostat

Computer

RE WE CE

N₂ in

N₂ out

0.5M H₂SO₄ + 0.5M CH₃OH (20ml)
RESULTS AND DISCUSSION
0.5M H₂SO₄ + 0.5M C₂H₅OH

PtSnIr/C method 1

Potential (V vs Ag/AgCl)

Current (mA)

-0.40 -0.20 0.00 0.20 0.40

-0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2

20mV/s 50mV/s 100mV/s

0.5M H₂SO₄ + 0.5M C₂H₅OH
0.5M H$_2$SO$_4$ + 0.5M C$_2$H$_5$OH

Potential (V vs Ag/AgCl)

Current (mA)

20mV/s
50mV/s
100mV/s

PtSnIr/C method 1
PtSnIrP/C method 2
PtSnIrP/C method 3

Current density (mA/cm$^2$)

Time (seconds)
0.5M H$_2$SO$_4$ + 0.5M CH$_3$OH

PtRuIr/C method 1

PtRuIrP/C method 2

Current (mA)

Potential (V vs Ag/AgCl)

20mV/s

50mV/s

100mV/s

Potential (V vs Ag/AgCl)
0.5M H$_2$SO$_4$ + 0.5M CH$_3$OH

PtRuIr/C method 1
PtRuIrP/C method 2
PtRuIrP/C method 3
Conclusions

• Electro-oxidation of methanol and ethanol takes place on electro-catalysts prepared.
• Kinetics of electro-oxidation reactions are different for various catalyst compositions
• Effect of P: high current density - improved performance
• Electro-catalyst performance depends on the preparation procedure
Future work

• Catalyst preparation
  - Optimize catalyst composition
    (Add Ir, P to Pt-Sn and Pt-Ru)

• Characterization:
  - Electrochemistry
    (Cyclic voltammetry, Impedance spectroscopy)
  - Structural and elemental analysis
    (TEM, EDX, XPS, ICP)

• MEA fabrication and performance tests in a unit fuel cell
  - Methanol and ethanol
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