dstl

DSTL/CP59314 1/13

Dstl is part of the
Ministry of Defence

[dstl]

A Direct Sodium Borohydride - Hydrogen Peroxide Fuel Cell Employing a Bipolar Membrane

Dr Robert Reeve

Power Sources Team, Dstl Porton Down, UK

Dstl is part of the Ministry of Defence

Introduction

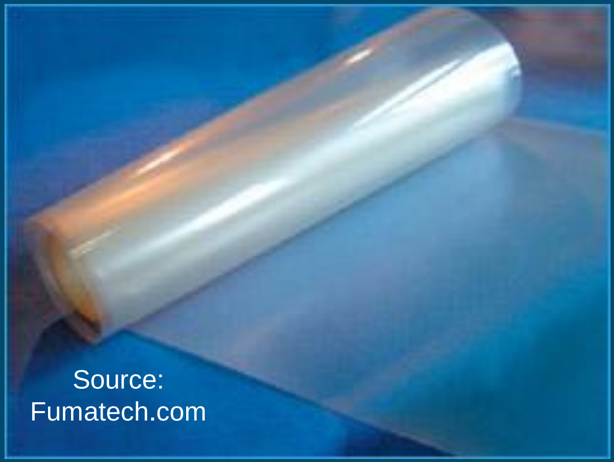
- This work addresses air-independent power
- It uses sodium borohydride as fuel and hydrogen peroxide as oxidant
- Approach based on a bipolar membrane concept
  - eliminates the storage of supporting electrolyte = high energy storage
- The benefits are air independent operation, emission free operation and low signature, constant mass and high specific energy
- Application areas include undersea vehicles and signature free surveillance systems

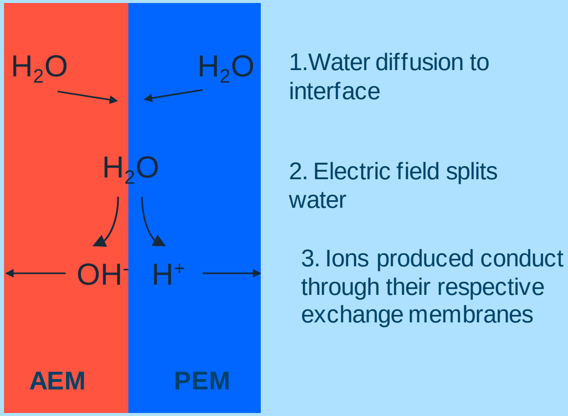
Bipolar membranes

- Layered combination of an anionic exchange membrane (AEM) and a proton exchange membrane (PEM)
- Passage of current creates an interfacial electric field sufficient to split water
- *In-situ* production of supporting electrolytes can be used for fuel cell reactions without weight burden of having to store them

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-$$

$$H_2O_2 + 8H^+ + 8e^- \rightarrow 8H_2O$$





Water splitting in a bi-polar membrane

Proposed system

- ***Anode***: Alkali catalysed oxidation of sodium borohydride

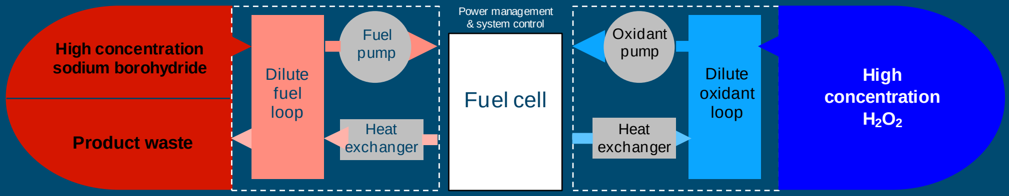
$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-$$

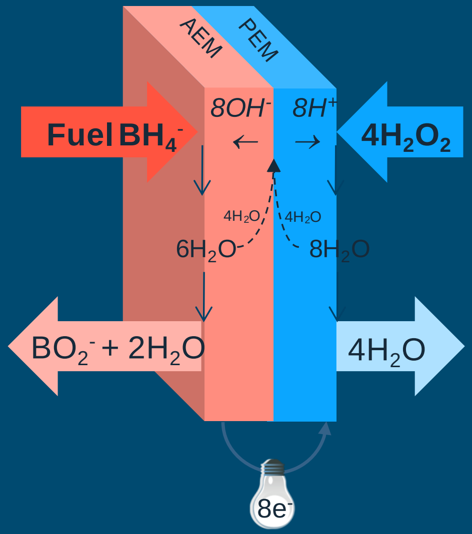
- ***Cathode***: Acid catalysed reduction of hydrogen peroxide

$$4H_2O_2 + 8H^+ + 8e^- \rightarrow 8H_2O$$

- OH^- and H^+ ions are produced from product water
- No need to store these in stoichiometric amounts

= higher energy storage

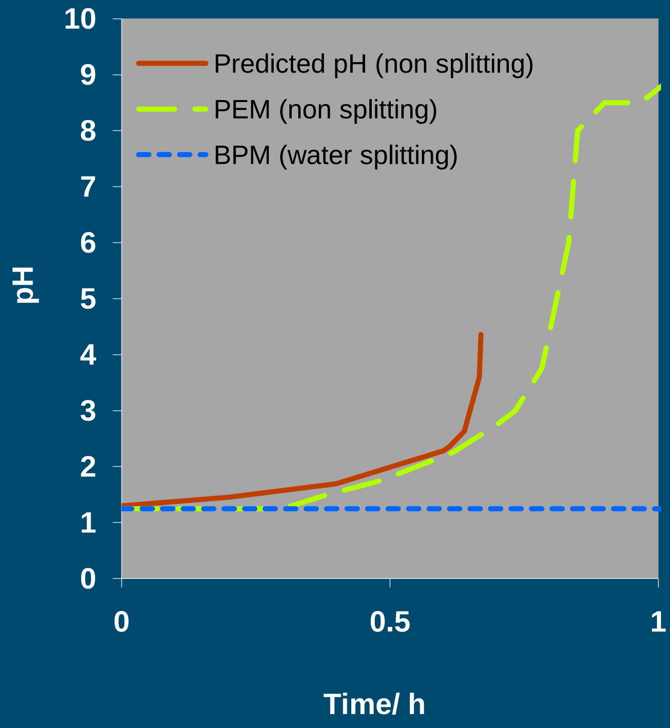




Proof of principle

The catholyte pH was monitored during a constant current discharge i.e., exhaustive electrolysis

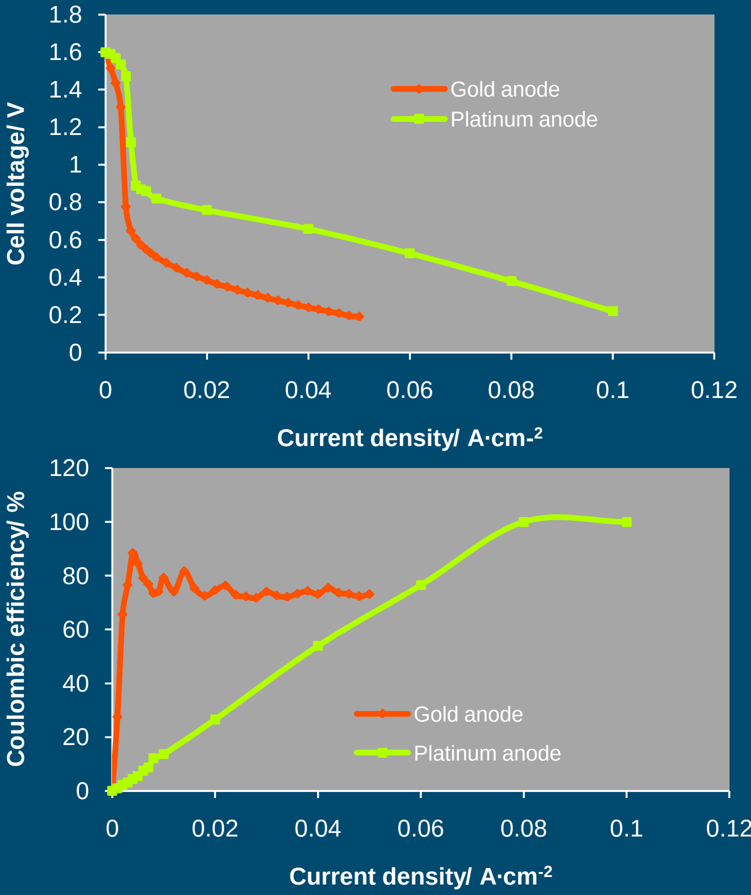
The pH did not increase with the BPM indicating that water splitting was replenishing the acid supporting electrolyte required for the hydrogen peroxide reduction process



$$H_2O_2 + 8H^+ + 8e^- \rightarrow 8H_2O$$

Anode catalysts

- Fuel utilisation is reduced by hydrolysis side reaction
  - $BH_4^- + 2H_2O = 2H_2 + BO_2^-$
- Catalyst and voltage specific
  - Gold/ carbon
    - low electrochemical activity
    - good efficiency at low outputs
  - Platinum/ carbon
    - high electrochemical activity
    - very high efficiency but only at high outputs



Polarisation characteristics and Coulombic anode efficiencies for a cell using different anode catalysts at 30°C.

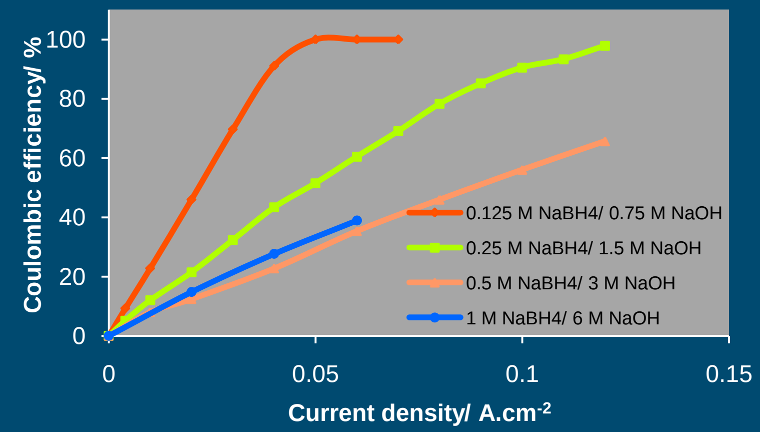
Fuel: 0.25 M $NaBH_4$ in 1.5 M NaOH

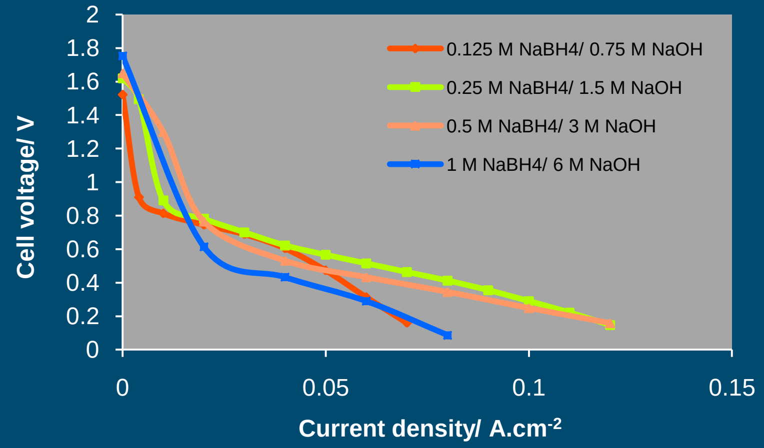
Oxidant: 3% H_2O_2 in 1 M H_2SO_4 (platinum)

fumasep® FBM membrane

Fuel composition

- Dilute fuel provides the highest fuel efficiency
- Efficiency increases to 100% at high current densities
- Overall compromise between efficiency and power density
  - – 0.25 M $NaBH_4$/ 1.5 M NaOH



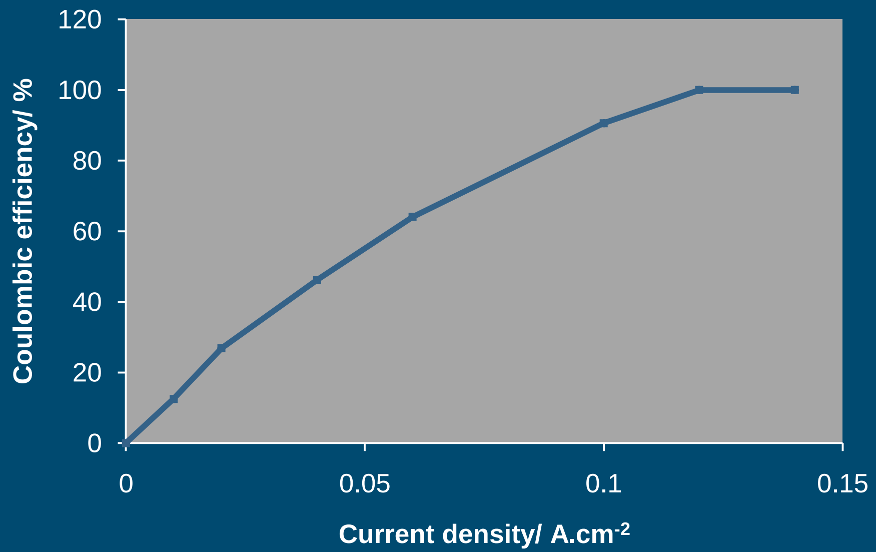


Polarisation characteristics and Coulombic anode efficiency for a cell operating with platinum based electrodes and a fumasep® FBM membrane at 30°C.

3% H_2O_2 in 1 M H_2SO_4

Cathode efficiency

- Hydrogen peroxide can decompose to produce oxygen
- Decomposition can be eliminated altogether but only at high fuel cell loads
- Platinum/ carbon used to date
- Silver for future consideration, including alternative support materials



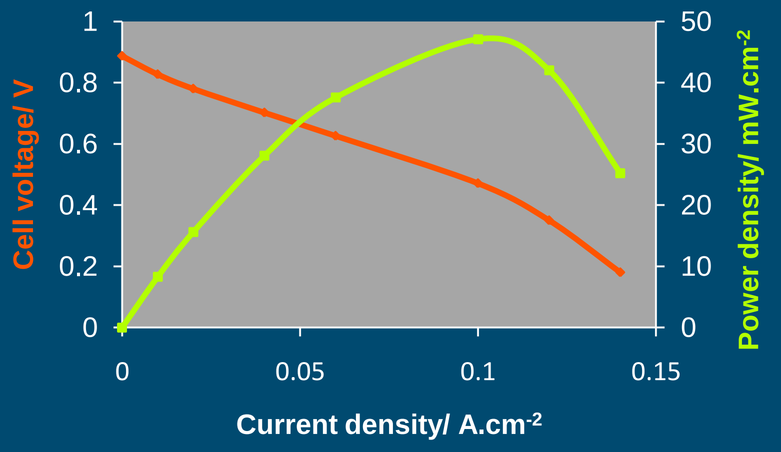
Coulombic efficiency for the reduction of hydrogen peroxide using a platinum based cathode at 30°C.

3% H_2O_2 in 1 M H_2SO_4

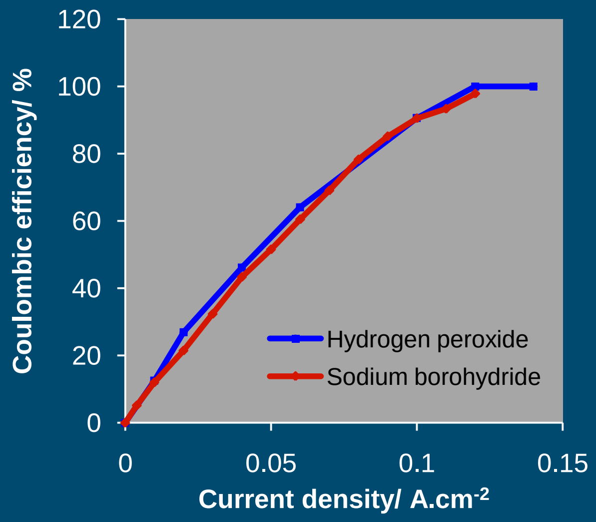
Dstl is part of the Ministry of Defence

System model

- For hypothetical 5 kW system operating for 100 hours
- Performance and efficiencies taken at 0.1 A·cm^{-2} operating point, as per figures opposite



Fuel concentration/ Wt%	Oxidant concentration/ Wt%	Specific energy/ Wh.kg^{-1}	
		Based on current performance Fuel cell = 128 kg	Target performance (150 mV improvement to anode and cathode) Fuel cell = 80 kg
10	80	147	240
25	80	244	397
30	80	263	428
Solid	80	364	590
Assumptions: 10% energy penalty for BOP. 20 kg for BOP. 95 Wt% liquid storage efficiency			



Further work

- Fuel management
  - Sodium borate has limited solubility and can precipitate if accumulated to high concentrations
  - This will need to be removed from the fuel loop to enable high concentration fuel solutions to be used i.e. > 10 wt % $NaBH_4$
- Improved power density
  - Catalyst and electrode formulations
  - Optimised BPM development

Conclusions

- A novel concept for an air-independent power system has been demonstrated. Based on two liquid reactants the system has application to undersea vehicles as well as other areas
- Bipolar membranes have been shown to provide pH balance for the electrode reactions, eliminating the requirement to store stoichiometric quantities of supporting electrolytes
- Work to date has achieved power densities in the region of 50 mW·cm^{-2} with Coulombic efficiencies for both anode and cathode reaction at or approaching 100%
- System level modeling indicates that this approach has potential for high energy

Near term	150 Wh·kg^{-1}	Current performance
Medium term	250 Wh·kg^{-1}	Current performance, advanced fuel management
Long term	425 Wh.kg^{-1}	Performance increment, advanced fuel management

DSTL/CP59314 13/13

Dstl is part of the
Ministry of Defence