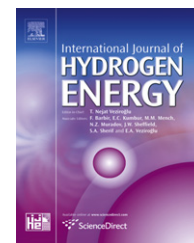


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# Prospects for alkaline zero gap water electrolyzers for hydrogen production

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## ABSTRACT

This review makes the case for cheaper and more efficient water electrolysis technology. In particular, the potential advantages of zero gap, alkaline water electrolyzers based on hydroxide ion conducting membranes are highlighted. Following a brief introduction into the thermodynamics and kinetics of water electrolysis, recent developments in oxygen evolving anodes, hydrogen evolving cathodes and hydroxide transporting membranes appropriate to such technology are reviewed.

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## 1. Introduction

Water electrolysis is not a new process for the production of hydrogen [1–11]; even 50 years ago, there were a number of industrial plants scattered around the world. Yet, water electrolysis remains a very minor contributor to the total production of hydrogen. In total, some 40 million tons of hydrogen are produced each year and used in the manufacture of ammonia, for the hydrogenation of organics, in petroleum refineries, in metals production, for electronics fabrication, for high temperature flames and for cooling thermal generators [12,13]. Presently, >95% of this H<sub>2</sub> comes from fossil fuel feedstock using high temperature, gas phase reactions such as



But, in contrast to the technologies based on reactions (1) and (2), water electrolysis provides a clean route to hydrogen from water and, if the electricity comes from renewable sources, the goal is achieved without the consumption of fossil fuel or the emission of CO<sub>2</sub> – truly green technology. Also, the hydrogen has a very high purity, >99.9% directly from the cell, ideal for some high value added processes such as the manufacture of electronic components.

Hydrogen provides a possible solution to our needs for a sustainable fuel for our future transport requirements and also an approach to the large scale storage of energy. Such scenarios would require a very large expansion in hydrogen production by water electrolysis and it is critical that the hydrogen is produced by green technology. The technology must, however, also be energy efficient and inexpensive. This provides a large driving force for new, improved water electrolysis technology. Existing water electrolysis plants are

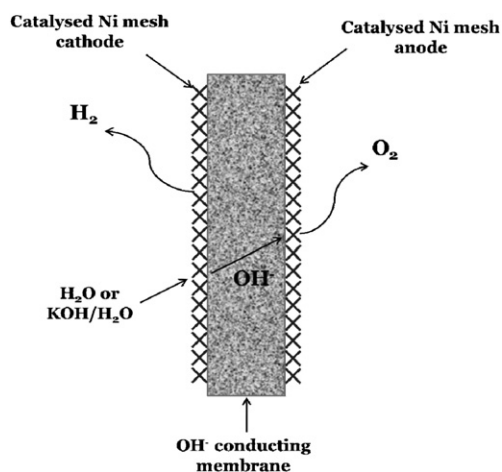
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usually based on cells with an aqueous alkaline electrolyte and a porous separator [14,15]. The maximum current density is typically  $\sim 0.25 \text{ A cm}^{-2}$  and even then its energy efficiency is typically only  $\sim 60\%$ . When combined with a fuel cell to provide a method of energy storage, the overall energy efficiency drops below 40%. These shortcomings led to the development of SPE (solid polymer electrolyte) cells with proton conducting membranes such as Nafion<sup>R</sup> as the electrolyte and either a zero gap configuration or cells with a fuel cell type membrane electrode assembly (MEA) [3,8,9,11]. While they lead to substantial improvements in the energy efficiency and they have been available, at least as small units, for at least 25 years, such electrolyzers have not impacted large scale  $\text{H}_2$  production. This is largely because of the high cost of both the membranes and the electrocatalysts in the acidic environment. In addition, water electrolysis cells that operate at elevated pressure are also marketed [4,7]; the major customers are the military and space exploration and the main product is commonly the pure oxygen for the atmosphere within submarines, space craft, etc. Hence, electrolyzers suitable for application on a very large scale but fabricated from cheaper components and achieving the essential reduction in cell voltage remains a highly desirable goal. Operation in alkaline conditions opens up the possibility of using non-precious metal electrocatalysts and anode materials in alkali can also give lower overpotentials for  $\text{O}_2$  evolution than in acid environments; cheaper cell components and lower energy consumption lead to the possibility of cheaper hydrogen production.

An attractive approach is based on the design of zero gap electrolyzers with a hydroxide conducting membrane, see Fig. 1. In such cells the electrodes are contacting the two membrane surfaces so as to minimise the voltage (IR) drop between the electrodes. While zero gap cells with a porous separator can be constructed, they are likely to have a higher voltage drop leading to operation at lower current density and, consequently, larger electrolysis plants. A hydroxide ion conducting membrane also offers the possibilities that (a) rather than being meshes or similar structures pressed



**Fig. 1** – Sketch of an alkaline water electrolyser based on an SPE (solid polymer electrolyte) cell with a hydroxide conducting membrane.

against the membrane, the electrodes can be fabricated directly onto the membrane surfaces to give a MEA familiar in fuel cell technology – the technology and fabrication of water electrolysis cells then becomes akin to that for alkaline fuel cells and (b) the cell feed is pure water rather than aqueous alkali since this simplifies auxiliary unit processes and reduces the possibility of corrosion in plant components. Stable, non-precious metal catalysts can be identified. The hydroxide conducting membrane needs to be stable and robust and fabricated from a polymer with a high conductivity for  $\text{OH}^-$  so that the cell can operate at a high current density (maybe  $1 \text{ A cm}^{-2}$ ). So far, it has been proved difficult to fabricate such membranes particularly membranes that operate well in contact with pure water and, indeed, it is uncertain whether suitable membranes are yet available on the open market. Acid membranes operate well with pure water feeds so that electron transfer appears to occur directly between the electrode materials and species within the polymer phase. Therefore, it is difficult to see why this problem with hydroxide conducting membranes cannot be solved. Certainly, several companies seem close to producing hydroxide ion conducting membranes with at least some of the required properties. Hence it seems timely to review the advances in alkaline zero gap technology resulting from the recent activity targeted towards upgrading water electrolysis technology. Particularly within energy storage, an attractive concept is the regenerative fuel cell [16,17] with the capability for the production of hydrogen and its conversion back to energy within a single cell; this of course requires an electrode composition and structure allowing energy efficient formation and consumption of both  $\text{O}_2$  and  $\text{H}_2$ .

The electrolysis of aqueous brine to give chlorine, sodium hydroxide and hydrogen remains the largest electrolytic process producing hydrogen. Indeed, chlor-alkali plants are ubiquitous throughout the world [4,18] and together produce  $\sim 1$  million tons per year of hydrogen despite it being considered a byproduct. But the economics of the chlor-alkali industry depend on the sale of the chlorine and sodium hydroxide as well as the hydrogen; expansion of hydrogen production on the scale being discussed would produce a vast excess of unsaleable chlorine. Moreover, at smaller installations away from chemical plant, the co-generation of chlorine would preclude it as a ‘green’ technology. In stark contrast to water electrolysis, however, the past forty years has seen a revolution in chlor-alkali technology with the development of both membranes and electrode catalysts specifically for the industry and the subsequent introduction of membrane cells. The same period has seen a massive activity related to proton conducting membrane fuel cells [19,20] and there have been substantial improvements in the performance of such fuel cells resulting from upgrading the cell configuration, the membrane and the electrocatalysts. The advances with respect to catalysts result from changes in composition and methods to disperse the catalysts over inert substrates, generally carbon based. They have led to significant reductions in catalyst loadings as well as lower overpotentials and greater stability to losses of both catalyst mass and catalyst surface area in operating conditions. While, unfortunately, the advances in chlor-alkali technology and proton exchange membrane (PEM) fuel cells may not be directly applicable to

water electrolysis, they certainly provide guidance as to how alkaline SPE technology might be developed.

## 2. Scaling our thinking

As we look to the future and consider water electrolysis for transport and energy storage application, it is critical that we understand the target being set. It will certainly be essential to have a buffer, based on electrochemical or other technology, between renewable sources of energy and the consumer; the renewable sources will produce energy only under favourable natural conditions (eg. during daylight, when the wind blows) while consumers expect to have access to electricity available at all times. On the other hand, it is necessary to recognise the scale of operations that is being discussed [13,21]. Table 1 compares the possible size of water electrolysis plants for various applications and compares it with some existing technology. The calculations shown in the table assume that all the electricity produced by the single power generation plant is to be stored and should be taken only as an indication of the demand for storage capacity. In the USA, however, there are the equivalent of 900 such power generation plants and, overall, it may be essential to have storage capacity equivalent to 30–50% of peak consumer demand in an ‘all renewable’ energy economy. This table also requires a number of assumptions about the current density of operation of a water electrolysis plant (in fact taken as  $0.5 \text{ A cm}^{-2}$ ), the way the car is used, etc and is intended only as a guide. There can, however, be no doubt about the conclusions. Firstly, the storage of energy by electricity generating companies through the generation of hydrogen will require the construction of plants much larger than any electrolysis plants presently in existence. In fairness, it should be recognised that a similar calculations based on batteries would be worse since water electrolysis cells operate at  $0.2\text{--}1.5 \text{ A cm}^{-2}$  while redox flow batteries are usually charged at  $<0.05 \text{ A cm}^{-2}$  and lithium ion batteries commonly below  $0.001 \text{ A cm}^{-2}$ . Less intensive storage looks more promising. A plant to store the electricity from a wind farm would appear more manageable. Although still a large electrolysis plant, it is one at least comparable to existing facilities; also it should be recognised that a large  $\text{Cl}_2/\text{NaOH}$  plant handles an equivalent amount of hydrogen, even

if it is considered the byproduct. For a fuel station to serve a small town, the scale technology becomes much more modest and it is possible to envisage the electrolysis in a single cell stack. To provide fuel for a single car, several companies can already provide a small unit to produce the hydrogen and the issues become safe storage and cost. Widespread adoption of electric vehicles would, however, also require some reinforcement of the local distribution network to handle the increased demand for electricity. All the future applications of water electrolysis will require improvements in energy efficiency, reliable, long lived and cheap cell components and innovation in cell design and manufacture.

The US National Renewable Energy Laboratory regularly reviews the economics of hydrogen production by water electrolysis and considers issues such as the integration of an electrolysis plant with a wind farm, for example [13,21]. It has been shown clearly that for small systems, the dominant factor in determining the cost of  $\text{H}_2$  is the cost of the electrolysis cells while, in contrast, for large systems the cost of electricity and the value of the hydrogen dominate the discussion.

## 3. Factors influencing the cell voltage

In order to convert water into hydrogen and oxygen, it is necessary to apply a voltage between two electrodes to drive the overall cell reaction



In alkaline solution, the corresponding cathode and anode reactions are



The cell voltage will have contributions from

- (a) the need to supply energy in order to drive the cell chemical change. Water is very stable at practical temperatures and hence there must be a significant energy

**Table 1 – Comparison of the scales of operation required for some proposed applications of water electrolysis and some present technologies. Reasonable values for current density, car usage, etc have been assumed. Note: the electric power generating capabilities are in the UK  $5 \times 10^4$  MW, USA  $8 \times 10^5$  MW and the world  $3 \times 10^6$  MW.**

	Power/MW	$\text{H}_2$ equivalent/ $\text{kg day}^{-1}$	Current/A monopolar	Electrode area/ $\text{m}^2$
Store electricity from a typical utility power plant	1000	$5 \times 10^5$	$5 \times 10^8$	$10^5$
Store electricity from a typical wind farm	50	$2.5 \times 10^4$	$2.5 \times 10^7$	$5 \times 10^3$
$\text{H}_2$ production facility for 2000 cars/day	2	$10^3$	$10^6$	200
Local storage for hotel or office block or group houses	0.2	100	$10^5$	20
Device to fuel a single car	0.02	1	$10^3$	0.2
Typical $\text{Cl}_2/\text{NaOH}$ plant	100	$2 \times 10^4$	$2 \times 10^7$	$6 \times 10^3$
Large $\text{H}_2\text{O}$ electrolysis plant	6	$3 \times 10^3$	$3 \times 10^6$	600

input to satisfy the thermodynamics of the unfavourable, overall chemical change, reaction (3).

- (b) the overpotentials to enhance the rates of the electrode reactions, reactions (4) and (5) to the desired high rate.  
 (c) to drive the current through the cell contacts, electrodes and interelectrode gap, whether aqueous electrolyte or membrane. The cell voltage is therefore given by an equation such as

$$-E_{\text{cell}} = \Delta E_e - |\eta_a| - |\eta_c| - IR \quad (6)$$

where  $\Delta E_e$  is the difference in the equilibrium potentials for the two electrode reactions,  $\eta$  are the overpotentials at the anode and cathode respectively,  $I$  is the cell current and  $R$  is the resistance of the cell. It should be noted that the overpotential and  $IR$  terms increase with current density and should be regarded as inefficiencies leading to low grade heat. Minimising the overpotentials depends on the availability of good electrocatalysts while minimising the  $IR$  term is dependent on good electrochemical engineering, ie. minimising the interelectrode gap, ensuring that only high ionic conductivity materials are between the electrodes and ensuring that the evolved gas effectively escapes the interelectrode gap.

The energy efficiency for the cell is given by

$$\text{Energy efficiency} = \frac{\Delta E_e}{E_{\text{cell}}} 100 \quad (7)$$

Typical values are in the range of 40–60% and the much of the present research and development seeks to increase the efficiency significantly as well as minimising the cost of the cell and all cell components.

#### 4. The thermodynamics of water electrolysis

In all water electrolysis cells operating below a temperature of 373 K, the overall chemical change is



The equilibrium lies far to the left – water appears completely stable. The conversion requires the input of energy and in electrolysis this is achieved by applying a potential difference between two electrodes. Under standard conditions where the temperature is 298 K and the gases are present at a pressure of 1 atm, the standard enthalpy,  $\Delta H^\circ$ , for reaction (8) is +286 kJ/mol of  $\text{H}_2$  and the Gibbs energy,  $\Delta G^\circ$ , is +238 kJ/mol of  $\text{H}_2$ . The significant difference arises because the electrolysis leads to the conversion of a liquid to two gases and hence to a large increase in the entropy of the system. In an isolated system, it would be necessary to apply a potential difference,  $\Delta E_e^\circ$ , of  $-1.48 \text{ V} (-\Delta H^\circ/4F)$  in order to satisfy the thermodynamic requirements. In practice, however, it is not necessary to introduce all the energy in the form of electrical energy and the increase in entropy can be achieved by absorption of heat from the surroundings (also, the inefficiencies in a practical cell, see above, will appear as heat that can contribute to this entropy gain). Then the potential difference required is then only  $-1.23 \text{ V} (-\Delta G^\circ/4F)$ . When operating away from standard conditions, the equilibrium cell

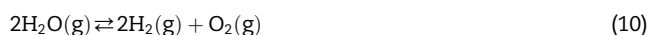
voltage must be calculated from the Nernst equations for the two electrode reactions and leading to

$$\Delta E_e = \Delta E_e^\circ + \frac{RT}{4F} \ln \frac{a_{\text{H}_2}^2 a_{\text{O}_2}}{a_{\text{H}_2\text{O}}^2} \quad (9)$$

where  $a$  are the activities of the reactant and products.

It should be noted that the thermodynamics of a water electrolysis cell are independent of pH. As can be seen from the Nernst equation for the two electrode reactions, the equilibrium potential for both the anode reaction and the cathode reaction shift negative with increase in pH at the same rate (both electrode reactions (4) and (5) involve  $1 \text{ H}^+/e^-$  and hence at 298 K, the shift will be  $-59.6 \text{ mV/pH}$  unit). Hence the difference in equilibrium potentials, the equilibrium cell voltage, is independent of pH. In fact this is immediately clear since the overall cell reaction, reaction (8), does not lead to the consumption or production of protons or hydroxide ion.

In addition, temperature has little influence on the thermodynamics. For example, at 353 K, a typical operating temperature for some cells, the equilibrium cell voltage is  $-1.19 \text{ V}$ , only a  $\sim 4\%$  decrease for a 55 K increase in temperature. Above 373 K, the cell reaction becomes



but, from the viewpoint of thermodynamics, the advantage of increasing the temperature remains small. For example, to obtain an equilibrium cell voltage of  $-1.00 \text{ V}$ , the temperature must be increased to 1000 K.

On the other hand, there may be good reason to increase the temperature. Higher temperature leads to substantially improved kinetics for both the electrode reactions and also an increase in the conductivity of the electrolyte, thereby decreasing  $IR$  drop. But the use of a higher temperature places more demands on materials – increasing the temperature will increase rates of corrosion and/or chemical decomposition and may also degrade mechanical properties.

#### 5. The kinetics of the electrode reactions

The rate (ie. current density,  $j$ ) of both the hydrogen and oxygen evolution reactions can be described by a Tafel type equation [22]

$$\log|j| = \log j_0 + \frac{|\eta|}{\beta} \quad (11)$$

where  $j_0$  is the exchange current density (ie. the equal, partial anodic and cathodic current densities at the equilibrium potentials),  $\eta$  is the applied overpotential ( $=E - E_e$ ) and  $\beta$  is the Tafel slope.

The kinetics of both hydrogen and oxygen evolution vary strongly with electrode material (electrocatalyst). The values of exchange current density vary by a factor of  $10^{10}$  while the variation of Tafel slope may lead to a variation of current density by a factor of 10 every 30 mV, 40 mV, 60 mV or every 120 mV (depending on mechanism) [23–29]. In consequence the overpotentials at each electrode can vary from  $<250 \text{ mV}$  to  $>2000 \text{ mV}$  at the operating current density of water



electrolysers. The performance of electrocatalysts certainly depends on the composition of the catalyst and its surface area but may also be a function of the catalyst microstructure (eg. the density of specific surface sites) and also the support for the catalyst.

In general, in this review, electrocatalysts will be compared using measured overpotentials at fixed current density. The use of exchange current density is avoided because the values in the literature are subject to large errors. In addition to factors such as pretreatments and experimental procedures, the determination of the exchange current density requires extrapolation of current density vs potential data over hundreds of millivolts using Tafel slopes that are poorly defined or even 'imaginary'.

The mechanisms and kinetics of both hydrogen evolution [23–26] and oxygen evolution [26–29] have been discussed extensively. In general, the kinetics of hydrogen evolution can be rapid so that the reaction takes place at many surfaces with only a small overpotential. In contrast, the kinetics of oxygen evolution are generally poor so that the anode reaction usually requires a substantial overpotential. Indeed, this overpotential is usually the major inefficiency in water electrolysis cells. The following two sections discuss hydrogen and oxygen evolution in conditions appropriate to an alkaline water electrolyser.

## 6. Cathodes

Hydrogen evolution is probably the most extensively studied electrode reaction [23–26]. While it is clear that the performance of cathode catalysts for this reaction depends on the composition of the catalyst, its microstructure and its surface area, it is possible to identify catalysts that allow efficient hydrogen evolution. In acid solution, the preferred materials are Pt or Pt alloys in a high area form, a metal black or metal nanocentres highly dispersed on a carbon powder support. One of the driving forces for the development of alkaline water electrolysers has always been the possibility of using cheaper, non-precious metal catalyst materials and this has not changed.

Unfortunately, however, the literature can be a poor guide to the performance of cathodes in operating water electrolysers. This is for several reasons. Firstly, much of the literature relates to room temperature whereas water electrolysers generally operate at 333–373 K where the rate of hydrogen evolution may be higher by a factor  $>100$ . The increased temperature alone may lead to a decrease in overpotential of maybe 200 mV. Secondly, because of concerns about IR distortion of experimental data, the kinetics of hydrogen evolution are generally discussed in terms of Tafel slopes and exchange current densities measured in a current density range ( $<0.01 \text{ A cm}^{-2}$ ) well below that employed for water electrolysis ( $0.2\text{--}2 \text{ A cm}^{-2}$ ) when it is possible that quite different mechanisms and kinetics operate. Indeed, the literature often proposes different Tafel slopes at 'low' and 'high' current densities although it is often unclear whether the conclusions result from the experimental difficulties of measuring reliable Tafel slopes at high current densities (eg. gas blanketing of the surface, IR drop). Thirdly, structure and

real surface area are as important as the composition of the catalyst layer in determining its activity; this is, of course, widely recognised but it still makes difficult the comparison of materials studied in different laboratories. Moreover, long-term stability and stability of performance are issues seldom addressed in the academic literature. In addition to corrosion (in all conditions met – ie. on-load, on open circuit and during switching out cells), the performance can be lost [30] due to (a) the absorption of hydrogen within the catalyst structure (b) the adsorption of organics (from impurities in the water/electrolytes or extracted from the membrane or polymer components) onto the catalyst surface or (c) deposition of metals (eg. Fe), less active as a catalyst, onto the cathode surface – such metal ions are most likely to arise from impurities in NaOH/KOH if the cell medium is aqueous alkali rather than pure water or corrosion of metal components in the electrolyser system. In this review, the discussion of cathode materials will focus only on those materials studied in conditions close to those found in an alkaline SPE water electrolyser. Much can be learnt from experience in the chlor-alkali industry [31] where commercial cathode coatings operate at low overpotential with lifetimes of several years. Zero gap cells are common and the cathode reaction is also hydrogen evolution in concentrated aqueous alkali at temperatures (333–363 K) similar to those employed in a water electrolyser. If the water electrolyser employs a NaOH/KOH medium, the conditions are virtually identical while if the medium is pure water the environment at the cathode remains similar, if perhaps less alkaline.

Traditional alkaline water electrolysers employ iron or steel cathodes but these are not sufficiently stable to corrosion at high alkali concentrations and elevated temperatures. Indeed, because of the adverse influence of Fe species in the catholyte, it is to be expected that water electrolysis cells will be fabricated from materials not containing iron. Certainly, the more expensive nickel is now universally used as the substrate material despite itself being a less active catalyst than iron or steel. Nickel is also a common component of the cathode coating. The Tafel slope for smooth nickel in KOH or NaOH solutions at room temperature is 120 mV indicating the initial electron transfer from the cathode to water molecules as the rate-determining step in hydrogen evolution [24,32]. The overpotential for hydrogen evolution is typically  $\sim 300\text{--}400 \text{ mV}$  at the current densities desired in water electrolysers, far too large for modern electrolysers and hence the focus needs to be on the development of electrocatalytic coatings. Nickel is also an example of a metal where absorption of hydrogen into the nickel lattice leads to deactivation although, fortunately, the increase in overpotential is much less at temperatures in the 343–373 K range. The influence of temperature on the kinetics of hydrogen evolution at nickel has been reported by several groups [33–35] and the overpotential for hydrogen decreases by  $\sim 200 \text{ mV}$  in going from 293 K to 363 K.

Even as early as 1980, the appropriate catalytic coatings for cathodes in a chlor-alkali membrane cell had been developed by commercial electrode manufacturers. Four types of coating were marketed (i) high surface area platinum or other precious metals [36–39] (ii) ruthenium dioxide [40,41] (iii) Raney Ni [42,43] and (iv) Ni alloys, particularly NiMo [39,44,45].

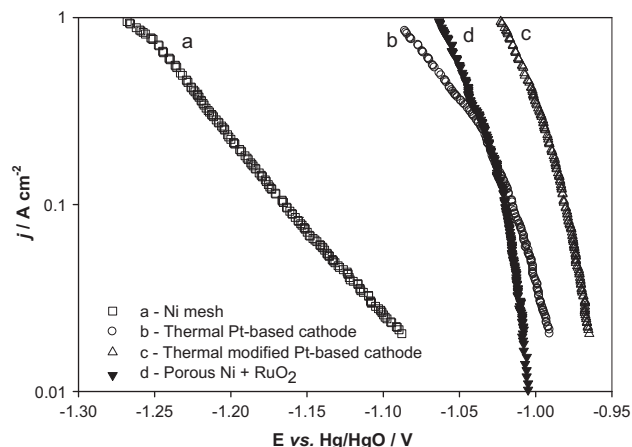
All claimed similar overpotentials for hydrogen evolution, 50–100 mV at a current density of  $0.5 \text{ A cm}^{-2}$ . As far as we are aware, all four types of coating can still be purchased although little specific information on the manufacturing technology or performance data has been published by the cathode suppliers.

It is, of course, generally, recognised that, at all pH, the precious metals are excellent catalysts for  $\text{H}_2$  evolution. In water electrolysis cells, the challenge is to present the precious metal(s) as a high area coating onto a nickel substrate in the form of a plate or, more commonly, a mesh and at an acceptable cost (ie. a low loading). Most commonly, the coating is deposited by electroplating or, more cheaply, by immersion plating using the Ni substrate itself as the reducing agent,



or by thermal decomposition of a sprayed platinum metal solution. Johnson Matthey [37,38] recommend a PtRu alloy with a loading of  $0.30\text{--}0.35 \text{ mg cm}^{-2}$  of Pt and  $0.1\text{--}0.15 \text{ mg cm}^{-2}$  of Ru, prepared by immersion plating. In common with all coating procedures, the Ni substrate is pre-treated; Johnson Matthey used a degreasing solution followed by sandblasting and acid etching. The coating was then applied in a single, room temperature operation by dipping the cathode into an acid solution of the precious metal chlorides. The adhesion of the coating is excellent. Initially, the overpotential for hydrogen evolution in 35% NaOH at 363 K is  $\sim 50 \text{ mV}$  at a current density of  $0.3 \text{ A cm}^{-2}$  but this rapidly rises to  $\sim 100 \text{ mV}$  unless the coating undergoes a post-treatment [38]. With precious metal cathodes, this rise in overpotential is commonly observed and has been attributed to poisoning by iron and/or organics [30]. Later, workers have used similar techniques to prepare Ru on Ni [46,47] and Ir on Ni [47] cathodes and undertaken more fundamental studies. They report overpotentials down to  $50 \text{ mV}$  at a current density of  $0.1 \text{ A cm}^{-2}$  even at room temperature and also Tafel slopes close to  $40 \text{ mV}$  to confirm that  $\text{H}_2$  evolution occurs via mechanisms involving H atoms adsorbed on the metal surface. They also report the advantage of using an electroplated Ni layer rather than a bulk metal substrate as this has a much higher surface area. Antozzi et al. [48] report performance data for some thermally prepared Pt coatings on nickel, see Fig. 2. These coatings are prepared following a commercial procedure and these Pt-based catalysts do show very low overpotentials.

The alternative approach to applying precious metals in water electrolysis cathodes is to use the precious metal dispersed over a high area carbon support in a fuel cell type electrode [19,20,28,49]. Usually the pre-prepared precious metal on high area carbon is mixed into an ink with other components such as PTFE (or Nafion for acid systems) and/or a surfactant in a solvent and applied (by spraying, brushing or screen printing) as a thin layer either directly onto the membrane or onto a carbon paper support. Practical gas diffusion electrodes may be multilayered structures with a gas diffusion layer formed from larger carbon particles so that it has larger pores as well as a catalyst layer. Up to now, this approach has not been common in SPE or zero gap alkaline water electrolysis cells but may become more



**Fig. 2 – Tafel plots for (a) Ni mesh (b,c) Pt-based cathodes prepared by thermal decomposition of Pt salts (d) Ni/RuO<sub>2</sub> nanoparticle composite in 10.4 M NaOH aqueous solution at 363 K. Data taken from [48]. Reproduced by permission of Elsevier.**

important as higher performance alkaline membranes become available.

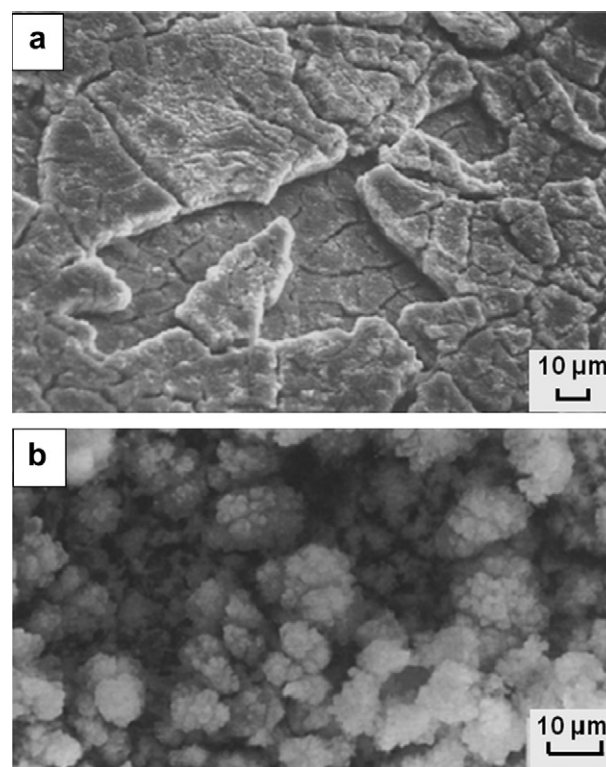
In practice, ruthenium dioxide is a very effective electrocatalyst for hydrogen evolution in alkaline solutions. At first sight, however, it is an unlikely candidate for practical application [41]. Firstly, examination of the Pourbaix diagram [50] shows that no oxide of ruthenium is thermodynamically stable at the potentials for  $\text{H}_2$  evolution. Secondly, one does not normally associate irreversible reactions with good catalysis;  $\text{RuO}_2$  layers neither take up the equilibrium potential of the  $\text{H}_2\text{O}/\text{H}_2$  couple when exposed to hydrogen or catalyse the oxidation of hydrogen because  $\text{H}_2$  is not dissociatively adsorbed on its surface. The stability of bulk ruthenium dioxide to reduction has been attributed to hydroxylation of the outer layers, thus producing a barrier layer only reducible at very negative potentials where high energy metallic species can be formed [51]. There is, however, clear evidence [41,51] from periodic cyclic voltammetry that a  $\text{RuO}_2$  layer does change during extended  $\text{H}_2$  evolution at its surface but the changes to the layer do not increase the overpotential for  $\text{H}_2$  evolution.

Ruthenium dioxide layers with high surface areas on nickel substrates are fabricated by three types of procedure (a) the thermal decomposition of alcohol solutions of  $\text{RuCl}_3$  [41,52] using methods familiar for the fabrication of dimensionally stable anodes [53] – such layers may also contain oxides of elements such as Ti, Nb, Zr to further improve their long-term stability, (b) the inclusion of  $\text{RuO}_2$  nanopowder into electroplated nickel [54–58] layer or (c) inclusion of  $\text{RuO}_2$  into a ruthenium layer formed by immersion plating [59]. In most cases, the Ni substrate is pretreated by sandblasting and acid etching. There is a general agreement that the  $\text{RuO}_2$  coatings give an overpotential for  $\text{H}_2$  evolution of  $<100 \text{ mV}$  at a current density of  $0.3 \text{ A cm}^{-2}$  in NaOH/KOH solutions at 363 K and that  $\text{H}_2$  evolution gives a Tafel slope in the range of  $30\text{--}60 \text{ mV}$ , most commonly  $40 \text{ mV}$ . Although not quite as active as fresh precious metal cathodes [48,59], eg. see Fig. 2, the performance

of ruthenium dioxide coatings is very stable over very long periods in conditions of  $H_2$  evolution. Its surface does not support the reduction of metal ions to metals and has a lower tendency than metal cathodes to adsorb organics. Also the coating is not harmed by the current reversals that can occur when the cell is taken off line [48,55,59].

Nickel had long been considered as a cathode material for water electrolysis and chlor-alkali cells. An obvious way to improve the performance of Ni based cathodes was to fabricate high surface area structures. Even sandblasting the surface of nickel leads to an  $\sim 50$  mV decrease in the hydrogen evolution overpotential over the current density range of  $0.1$ – $1.0$   $A\ cm^{-2}$ . With the application of Raney nickel, a much larger improvement was found and the 1970s and 1980s saw a substantial number of publications [24,34,60–62]. Such cathodes have been prepared by methods such as sintering and electroplating but the most successful method involves the encapsulation of NiAl or NiZn nanopowder in an electroplated Ni layer after which the Al or Zn dissolves in KOH/NaOH electrolyte to give a very high area surface; oxides of metals such as Ti, Zr and Nb have been added to improve the properties of the layer. Such electrodes gave a decrease in overpotential compared to smooth Ni of  $\sim 200$  mV with overpotentials of  $\sim 100$  mV at  $0.3$   $A\ cm^{-2}$ . The Tafel slope also decreased from 120 mV on smooth Ni to 40 mV on Raney Ni; the mechanism is changing to one where adsorbed hydrogen is an intermediate. Tanaka et al. [63] have reported the influence of the Ni:Al ratio in the Raney Ni and find the lowest overpotential for  $H_2$  evolution when there is a high Al content. Raney Ni electrodes are not stable to current reversal on taking a cell off load but Yoshida and Morimoto [64] have proposed a more complex structure where both a Raney Ni alloy powder and a  $H_2$  absorbing alloy powder were occluded into an electroplated Ni layer. Such surfaces gave a further slight decrease in overpotential but also protected the layer from current reversal. The oxidation of the  $H_2$  adsorbed in the alloy occurs preferentially to the oxidative dissolution of the nickel on current reversal and hence avoids loss of surface area leading to a higher overpotential.

While molybdenum shows some tendency to dissolve in hot, concentrated KOH/NaOH, NiMo alloys are thought to have additional mechanisms for catalysis of hydrogen evolution, over and above formation of a porous Raney nickel structure. The 1980s again saw intensive studies of NiMo electrocatalyst layers [24] and surfaces were prepared by thermal decomposition followed by hydrogen reduction [34,44,45], electrodeposition of NiMo layers [65–67] sometimes as a NiMoCd alloy as this gave a high surface area [67], ball milling of Ni and Mo nanopowders to form alloy particles followed by pressing to give an electrode [68,69] and low pressure plasma spraying of NiAlMo alloy powders followed by leaching [70–72]. The papers by Brown et al. [44,45] suggest that their alloy coating prepared by thermal decomposition and reduction contained 13% Mo. The coating had a face centred cubic structure with random replacement of Ni atoms by Mo atoms where the mean lattice parameter was 0.358 nm compared to 0.352 nm for pure nickel. SEM showed the layer to have a ‘cracked, dried mud’ appearance, see Fig. 3(a) unchanged by very long electrolysis (3000 h) at  $0.5$   $A\ cm^{-2}$  in 30% NaOH at 343 K [67]. Other preparations lead to layers with

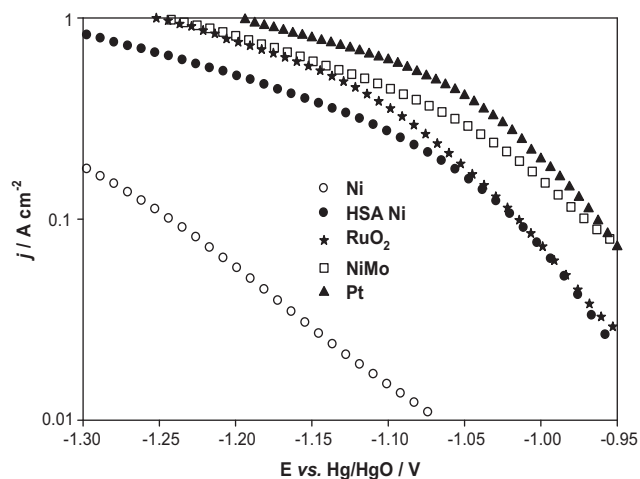


**Fig. 3 – Scanning electron microscope images of the NiMo electrocatalyst layers produced by (a) spraying the Ni substrate with aqueous Ni(II) and molybdate solution, thermal decomposition and hydrogen reduction [67] (b) low pressure plasma spraying of NiAlMo powder and activation in aqueous alkali [70]. Reproduced by permission of Springer.**

quite different morphologies (the low pressure plasma spraying of NiAlMo alloy followed by leaching led to a ‘cauliflower’ morphology, see Fig. 3(b) [70]) but similar overpotentials for  $H_2$  evolution were observed and the Tafel slopes were 40–60 mV. The papers by both Brown et al. [44,45] and Schiller et al. [71] confirm the outstanding performance of the NiMo alloys. Overpotentials are very low,  $\sim 60$  mV at  $0.5$   $A\ cm^{-2}$  in 30% NaOH at 343 K and this performance is maintained over many thousand hours even when the regime includes switching out the cell and variation of the current load. Hu et al. [73,74] have, however, advocated inclusion of a hydrogen absorption alloy in the coating to act as a buffer to current reversal on switching out the cell. NiMo alloys certainly seem to be the cathode electrocatalyst of choice for alkaline water electrolyzers particularly if precious metals are to be avoided.

In order to consider their suitability in zero gap electrolysis cells with a hydroxide conducting membrane, Li and Pletcher [75] have compared the performance of several cathode materials, see Fig. 4. The cathode coatings were a commercial  $RuO_2$  coating and high surface area Pt, Ni and NiMo coatings deposited using sputtering on a fine Ni mesh and these are compared with the uncoated mesh in the figure. In 4 M NaOH at 333 K, the Pt cathode again shows the best performance but both the  $RuO_2$  and the alloy coatings are almost as good and all





**Fig. 4** – Tafel plots for hydrogen evolution at various coating materials in 4 M NaOH at 333 K.

allow current densities in excess of  $1 \text{ A cm}^{-2}$  with only a moderate overpotentials. The Ni containing materials showed no significant increase in overpotential over a 10 day period but Pt showed an increase of 150 mV over a 1 day timescale when tested in a zero gap electrolysis cell with a hydroxide conducting membrane, probably due to adsorption of trace organics in the system.

## 7. Anodes

The overpotential for oxygen evolution at the anode is always large compared to the overpotential at the cathode. No electrocatalysts developed up until now can be considered entirely satisfactory and, in consequence, there remain intensive efforts into developing lower overpotential and more stable electrocatalysts for oxygen evolution. Because of the significant overpotentials required for both oxygen evolution and oxygen reduction, even at the best electrocatalysts, the potential for anodic oxygen evolution is substantially positive to that for cathodic oxygen reduction. This has two consequences (a) even materials nominally discussed as metals are, in fact, covered by an oxide layer (b) at the more positive potential, the driving force for corrosion is higher and corrosion of both the electrocatalyst and the catalyst support are major concerns for water electrolysis cell technology (even when they are stable in fuel cell cathodes). In addition, because of this difference in potential and the complex mechanisms involved in oxygen evolution/reduction (unlike hydrogen evolution/oxidation) the electrocatalysts for oxygen evolution and reduction can be very different.

For the same reasons as stated at the beginning of the section on cathodes, the vast academic literature [11,26–29,41] on anodes for oxygen evolution is, at best, a guide. It is, however, clear that (a) the kinetics of oxygen evolution are never fast (b) it is a complex, multistep reaction involving at least four electron transfers and four proton transfer steps (c) the overpotential for oxygen evolution can depend strongly on the anode material, surface state and temperature. In this review, the focus will be on material for

alkaline cells at temperatures in the range of 333–393 K and able to support current densities  $>>0.5 \text{ A cm}^{-2}$ . Even with this limited goal, differences in experimental procedures make difficult comparisons between papers; different groups use different reference electrodes and conversions to other scales while the working electrodes vary from well constructed gas diffusion electrodes to electrode coatings fabricated using diverse procedures.

One major advantage of alkaline conditions is that non-precious metal materials including nickel, cobalt and steels, can be stable. Moreover, in early work [76,77], precious metals were reported to have little or no superiority to nickel for oxygen evolution in alkaline solution. When Pt, Pd, Rh, and Ni were electrodeposited onto Ni foam and the resulting coatings tested in a water electrolysis cell at a current density of  $0.2 \text{ A cm}^{-2}$  in 30% KOH electrolyte at 363 K, the cell voltages were Rh (1.72 V), Pd (1.74 V), Ni (1.75 V), and Pt (1.80 V). Miles et al. [77] reported about equal activities for Ir, Pt, Rh, and Pd electrodes while suggesting that Ni was slightly better. In later work [78], they prepared various precious metal oxide electrodes by a thermal decomposition method and found that in 30% KOH at 353 K the effectiveness of these oxide electrodes for oxygen evolution decreases in the order  $\text{Ru} > \text{Ir} \sim \text{Pt} \sim \text{Rh} \sim \text{Pd} \sim \text{Ni} \sim \text{Os} \gg \text{Co} \gg \text{Fe}$  with Tafel slopes ranging from 46 to  $191 \text{ mV dec}^{-1}$ .

Precious metal (Ru, Ir) alloys with nickel have also been studied [79] but the decrease in overpotential for oxygen evolution compared to nickel is small and the use of such alloys is unlikely to warrant the additional cost. In addition, it was found that after long-term electrolysis, the surface film was largely nickel oxide, independent of the bulk alloy composition. The precious metal oxides dissolved in the alkaline medium.  $\text{RuO}_2$  and  $\text{IrO}_2$  exhibit good electrocatalytic activity for oxygen evolution and are generally the electrocatalysts of choice in acid solutions but there are doubts about their stability in alkaline media as they suffer slow dissolution in alkaline solution [28,80]. Also, thermal treatment [81] or addition of  $\text{Ta}_2\text{O}_5$  [82] has been suggested to improve their lifetime in acid solution but such modifications have not been examined in alkaline solution.

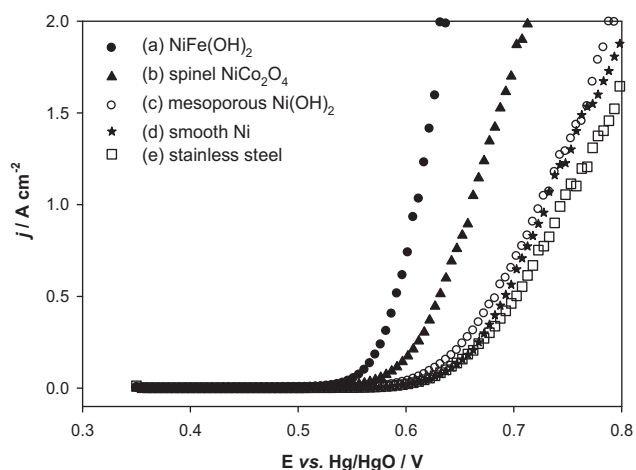
Pyrochlore-type and delafossite-type oxides containing precious metal have demonstrated outstanding activities towards oxygen evolution in alkaline solution. Pyrochlore-type oxides have the general formula  $\text{A}_2[\text{B}_{2-x}\text{A}_x]\text{O}_{7-y}$ , where  $\text{A} = \text{Pb}$  or  $\text{Bi}$ ,  $\text{B} = \text{Ru}$  or  $\text{Ir}$ ,  $0 < x < 1$  and  $0 < y < 0.5$ . Horowitz and coworkers [83] report that the pyrochlore oxide  $\text{Pb}_2[\text{Ru}_{1.67}\text{Pb}_{0.33}]\text{O}_{6.5}$  displayed a very low overpotential for oxygen evolution in 3 M KOH at 348 K with better performance than Pt black,  $\text{RuO}_2$ ,  $\text{NiCo}_2\text{O}_4$  and Ni sheet. The electrocatalyst also showed reasonable activity maintenance over long periods (500–1800 h) of oxygen evolution at current densities  $0.025\text{--}0.1 \text{ A cm}^{-2}$ . Other promising pyrochlores include  $\text{Pb}_2(\text{Ir}_{1.67}\text{Pb}_{0.33})\text{O}_{6.5}$  and  $\text{Nd}_3\text{IrO}_7$  [84]. The pyrochlores give a low Tafel slope, 24–40  $\text{mV dec}^{-1}$  and their high activity of these oxides was explained in terms of their oxygen deficiency. Delafossite-type oxides also show activity for oxygen evolution [85] decreasing in the order  $\text{PtCoO}_2 > \text{PdCoO}_2 > \text{PdRhO}_2 > \text{PdCrO}_2$ .

Electrocatalysts based on nickel and/or cobalt (high area metal, oxide/hydroxide layers, spinels, perovskites) generally



outperform precious metal materials in terms of both overpotential and stability as well as being lower cost. In early work, Hall [86,87] confirmed the advantage of using Ni metal in a high area form. The coating was fabricated by sintering a Ni powder (prepared by the thermal decomposition of nickel tetracarbonyl) onto a steel substrate. Anodes prepared in this way had an oxygen evolution overpotential of 250 mV at  $0.4 \text{ A cm}^{-2}$  in 30 wt% KOH at 353 K and a Tafel slope of  $\sim 35 \text{ mV dec}^{-1}$ . They also gave a stable performance, the anode potential being essentially constant for 1200 h at  $0.1 \text{ A cm}^{-2}$ . The author suggested that the anode can be stabilised by formation of a protective nickel–iron alloy layer at the steel surface, resulting from nickel diffusion into the steel during sintering. The effective surface area of nickel anode can be further increased by impregnation of the porous structure with nickel hydroxide via electrochemical precipitation methods [88]. Such procedures lowered the oxygen evolution overpotential by a further 45–60 mV with a preferred  $\text{Ni(OH)}_2$  loading of  $1\text{--}4 \text{ mg cm}^{-2}$ .

Another successful approach to obtaining a low overpotential involves the use of mixed transition metal oxide/hydroxides particularly iron-doped nickel hydroxide composites [89–93]. Corrigan [89] first reported that co-precipitation of iron into nickel hydroxide thin films dramatically improved the catalysis of the oxygen evolution reaction. A substantial contribution arises from the lowering the Tafel slope from about  $70 \text{ mV dec}^{-1}$  with no iron present to about  $25 \text{ mV dec}^{-1}$  with 10–50 wt% iron. The oxygen overpotential on thin films of  $\text{Ni-Fe(OH)}_2$  electrodes was over 200 mV lower than that with nickel hydroxide itself at  $0.08 \text{ A cm}^{-2}$  in 25 wt% KOH at 296 K. The enhanced electrocatalytic activity of iron-doped nickel hydroxide composites for oxygen evolution was later confirmed by other researchers [91–93]. Li et al. [93] compared a number of nickel based coatings, see Fig. 5,



**Fig. 5 – Steady state polarisation curves recorded at various coating materials in 1 M NaOH at 353 K: (a) a mixed Ni/Fe(OH)<sub>2</sub> layer deposited from the sulphate solution using a cathodic current density of  $0.25 \text{ A cm}^{-2}$  for 50 s; (b) a  $\text{NiCo}_2\text{O}_4$  spinel prepared thermally from a nitrate medium containing both Ni(II) and Co(II); (c) a mesoporous  $\text{Ni(OH)}_2$  layer; (d) a polished nickel microdisc and (e) a polished stainless steel microdisc [93]. Reproduced by permission of the Royal Society of Chemistry.**

including a spinel and concluded that a cathodically prepared Ni–Fe hydroxide coating was the anode of choice for a zero gap alkaline water electrolyser.

It has been known for over 30 years that spinel oxides are effective anodes for oxygen evolution with promising long timescale performance [94]. Tseung et al. [95–98] pioneered the use of  $\text{NiCo}_2\text{O}_4$  and pure or Li-doped  $\text{Co}_3\text{O}_4$ . Teflon-bonded  $\text{NiCo}_2\text{O}_4$  electrodes gave over  $1.3 \text{ A cm}^{-2}$  at an overpotential of 400 mV in 5 M KOH at 343 K and endured long-term oxygen evolution at  $1 \text{ A cm}^{-2}$  at 358 K in 45 wt% KOH for 3000 h with less than 50 mV increase in overpotential. Similar performance was observed by Vandenborre et al. [99] who developed a zero gap alkaline water electrolyser based on an alkali-compatible ion exchange membrane. Among the tested anodes including Ni,  $\text{NiCo}_2\text{O}_4$ ,  $\text{NiCoO}_2$ , and  $\text{La}_x\text{CoO}_3$ ;  $\text{NiCo}_2\text{O}_4$  spinel oxide showed the best performance up to 393 K in 50 wt% KOH for 2000 h operation. The tested  $\text{NiCo}_2\text{O}_4$  electrodes were prepared by thermal decomposition of nickel and cobalt salts on perforated nickel plates.

Tseung et al. [98] also reported that Li-doped  $\text{Co}_3\text{O}_4$  was a superior catalyst to  $\text{NiCo}_2\text{O}_4$  with a Teflon-bonded Li-doped  $\text{Co}_3\text{O}_4$  electrode giving  $1 \text{ A cm}^{-2}$  at an overpotential of  $\sim 300 \text{ mV}$  in 5 M KOH at 343 K. Moreover, long-term durability tests carried out on this electrode under practical conditions (at  $1 \text{ A cm}^{-2}$  in 45 wt% KOH at 358 K) showed good stability of performance for 5800 h. In contrast, Bocca et al. [100] observed a general decay on these electrodes performance subjected to galvanostatic electrochemical ageing for 21 days at  $0.15 \text{ A cm}^{-2}$  at 333 K, but pointed out that parameters in the fabrication of the electrodes leading to different oxide morphology and Teflon contents could lead to this difference.

During the last three decades, considerable effort has been made to enhance the performance of spinel-type oxides for oxygen evolution by (i) the development of new preparative methods to achieve high active area and (ii) partial substitution of constituent metal ions of the oxide by other similar metal ions. The developed preparation methods include thermal decomposition [94,98–100], freeze drying method [97], sol–gel method [101,102], vacuum evaporation [103], chemical spray pyrolysis [104], electrophoretic deposition [105], and hydroxide co-precipitation method [106] etc. Various ternary spinel oxides have been studied and shown promising activity towards oxygen evolution [107–110].

Perovskites are a family of oxides having a crystal structure similar to that of the mineral perovskite  $\text{CaTiO}_3$  and have a general chemical formula  $\text{ABO}_3$  [111], where A is a larger cation (such as La, Sr, and Nd) and B a small transition metal cation (such as Ni, Co, Fe, Mn, etc). They are usually prepared by thermal decomposition of an appropriate mixture of metal salts or by the solid state reaction of metallic oxides and they possess high electronic conductivity which is favourable for electrochemical catalysis. Matsumoto et al. [112–116] have reported investigations of several perovskite-type oxides including  $\text{SrFeO}_3$ ,  $\text{SrFe}_{0.9}\text{Mn}_{0.1}\text{O}_3$ ,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ,  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ , and  $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$  as anodes for oxygen evolution in alkaline solutions. The catalytic performance is reasonable but probably not as good as the spinels and the mixed transition metal oxide/hydroxides. Moreover, slow dissolution of  $\text{SrFeO}_3$  was observed in the conditions for oxygen evolution in alkali [112] although this problem may be overcome by doping

other transition metals into the structure to form  $\text{SrFe}_{0.9}\text{M}_{0.1}\text{O}_3$ , where  $M = \text{Ni}, \text{Co}, \text{Ti}, \text{or Mn}$ . Indeed, the anodic dissolution is much suppressed by the substitution with Ni or Co ion [114]. Detailed studies on mechanism for oxygen evolution reaction on  $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$  series oxides show that the rate of the oxygen evolution reaction increases with the increases of  $x$  and  $y$ , and  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.2}\text{Co}_{0.8}\text{O}_3$  is the best electrocatalyst of the oxides investigated [116]. Bockris and Otagawa [117–119] used voltammetric techniques with eighteen perovskites and correlated the electrocatalytic properties of perovskites for oxygen evolution with their electronic structures, with stress upon the characterisation of the bonding of surface oxygenated intermediates. Using Tafel slopes and reaction orders for oxygen evolution they proposed a common mechanism involving the electrochemical adsorption of  $\text{OH}^-$ , followed by the rate-determining electrochemical desorption of OH and catalytic disproportionation of the  $\text{H}_2\text{O}_2$  to give  $\text{O}_2$ .  $\text{LaNiO}_3$  gives the highest electrocatalytic activity among the perovskites studied and exhibits a stable performance for over 70 h at  $0.1 \text{ A cm}^{-2}$  in 1 M NaOH at 298 K.

In more recent work, Singh and coworkers [120–125] have worked further on perovskite anodes. They synthesised the oxides by low temperature routes such as malic acid aided sol–gel method and carbonate precipitation. The oxides were active for oxygen evolution compared to similar electrodes obtained by other methods. For instance, the oxygen overpotentials observed on  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  electrode in 30 wt% KOH at 343 K were 305 and 340 mV at 0.5 and  $1 \text{ A cm}^{-2}$ , respectively [120,121].

While usable electrocatalysts have been defined, the last word on oxygen evolving anodes has not been said. The demand for higher performance remains and new compositions will continue to be tested. It is also clear that the method of catalyst preparation as well as the structure of the anode tested influence both catalytic activity and the stability of the materials.

## 8. Membranes supporting hydroxide transport

As noted in the discussion of Fig. 1, a preferred design of alkaline water electrolyser would have a hydroxide conducting membrane with a low resistance and hence permitting water electrolysis at current densities around or above  $1 \text{ A cm}^{-2}$  with only a small IR loss. The membrane polymer must also be stable and it would be advantageous if the cell medium was pure water rather than an alkaline electrolyte. When the electrodes are with the membrane fabricated into an MEA, the cell structure becomes closely similar to an alkaline fuel cell. Hence the literature on alkaline fuel cells becomes very relevant to the future of alkaline water electrolysis technology.

For many years, anion permeable membranes have been available commercially from companies such as Ionics [126], Tokuyama [127] and Fuma-Tek [128]. In general, however, these membranes were intended for electrodialysis and targeted towards the transport of anions other than hydroxide; they were not stable to high pH conditions. Advances in

hydroxide permeable polymers were necessary for the development of the bipolar membranes used in the recovery of acids and bases from salt solutions [129–131]. Even these polymers were, however, only stable to hydroxide in modest conditions ( $< 2 \text{ M OH}^-$ , below 323 K, low current densities) and therefore unsuitable for application in water electrolysers (or fuel cells) where the target is to operate at temperatures up to 363 K, current densities in the range of  $0.5\text{--}2.0 \text{ A cm}^{-2}$  and often requiring stability to highly alkaline conditions. Recent years have seen substantial efforts to develop membranes with the properties required for water electrolysers and fuel cells [132,133].

It is not difficult to synthesise polymers with fixed cationic groups, designing structures with stability to attack by hydroxide at a high pH and elevated temperatures is a problem. Why has it proven difficult to design hydroxide conducting membranes with a low resistivity? There are a number of reasons:

- (i) In most media, the transport of hydroxide is a slower process than the transport of protons and in order to obtain low resistances similar to those readily obtained for proton conducting membranes, the hydroxide conducting polymers need to have a high density of fixed ionic groups. Such polymers often have poor flexibility and mechanical integrity. This leads to the need to introduce a reinforcing mesh or a neutral copolymer in order to improve the physical properties of a membrane and commonly such neutral polymers are not stable to strong alkali at elevated temperatures.
- (ii) The most successful proton conducting membranes are based on perfluorinated polymers with sidechains containing sulfonate groups (most notably, Nafion<sup>®</sup> supplied by Dupont) and such ionic polymers have outstanding stability to all aqueous media. Such an anion conducting membrane was once marketed (Tosflex<sup>®</sup> SF17, Tosoh Corp.), but its cost was prohibitive and it was withdrawn from sale. Other ways to introducing cationic centres into perfluorinated polymers have not yet led to commercial membranes.
- (iii) In addition, in almost all hydroxide conducting polymers, the fixed ionic group is a quaternary ammonium group ( $-\text{NR}_2\text{H}^+$  groups are rapidly deprotonated in strong base) and clearly these must be stable to attack by hydroxide. Hydroxide ion is a nucleophile and leads to loss of fixed ionic groups via two types of mechanism. When the polymer structure includes a hydrogen atom bonded to the carbon  $\beta$  to the positively charged nitrogen, Hoffman elimination occurs leading to a vinyl group attached to the polymer and the release of tertiary amine or release of an alkene and a tertiary amine centre as the fixed group. In the absence of such hydrogen atoms, direct nucleophilic attack on the charged nitrogen centres can lead to the loss of an alkyl group as an alcohol and again the formation of a neutral fixed tertiary amine group. The Hoffman elimination is the more rapid chemistry and hence the polymer is usually of the type polymer  $-\text{A}-\text{N}(\text{CH}_3)_3^+$  where A has a structure without  $\beta$ -hydrogen atoms and designed to minimise the rate of nucleophilic attack on the charged nitrogen centre itself.

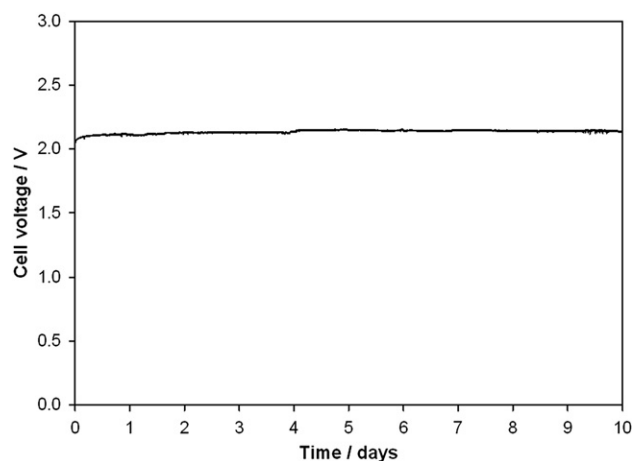
Some hydroxide conducting polymers only show promising performance in water electrolysis cells when in contact with concentrated aqueous alkali. This is a disadvantage since the presence of alkali increases corrosion of metal components and limits the materials that can be used both within the cell and the auxiliary equipment. While it is evident that the absence of alkali contacting the membrane/electrode structure leads to a substantial increase in cell voltage, it is not clear whether the problem lies in the membrane polymers themselves or with the contact/interface between the electrodes and polymer. It would be interesting to investigate the pH seen by the electrode surfaces in contact with alkaline membranes since it may not be as high as the electrocatalysts desire. In acid membrane water electrolysis cells the same problem does not occur and the cells are usually water fed. Similarly, PEM fuel cells with acid membranes operate with wet gas feeds without problem. The acid polymers are, however, strongly acidic and are used as acid catalysts in organic synthesis. Also Nafion solution is a common constituent of electrode inks and the equivalent solutions of hydroxide conducting solutions may not yet exist. While pure water electrolyzers remain the long-term goal, at the present stage, high performance, zero gap alkaline electrolyzers are of great interest.

The past ten years have seen a large academic effort into the development of new hydroxide conducting polymers with low resistance. This work has involved three general approaches. The first involves radiation grafting fixed ionic groups into an existing polymer sheet. The polymer sheet can be either a perfluorinated, partially fluorinated or non-fluorinated polymer. It is soaked in a precursor molecule such as vinylbenzyltrimethyl-ammonium chloride and then exposed to  $\gamma$  irradiation or an electron beam to convert the precursor into active radicals. This approach is well illustrated by the papers published by Slade and coworkers [132–138]. The second approach has been based on the synthesis of ionic polymers with chemistries different from the traditional poly(styrene/divinylbenzene) copolymers. A common selection of polymer backbone has been a poly(arylene sulfones) [139–143] or poly(arylene ether sulfones) [144,145] and the exact structure of the backbone, the nature of the cationic fixed ionic groups and the extent of crosslinking have each been varied. Also, some groups have reported totally new synthetic routes using designed monomers, eg., substituted cyclooctenes [146]. The final approach has used poly(-benzimidazole) filled with aqueous KOH [147–150]. While all three approaches have yielded polymers stable to strong alkali and moderate conductivities, none have sufficient conductivity to allow water electrolysis cell operation at current densities  $>0.1 \text{ A cm}^{-2}$  with an acceptable membrane IR drop. The IR drop across the membrane is, of course, a function of the membrane thickness as well as the polymer conductivity. Thus membranes with thicknesses down to  $10 \mu\text{m}$  can be considered but this makes the membranes difficult to handle during the construction and/or servicing of cells.

In parallel, it is clear that a number of companies have been seeking anion membranes appropriate for alkaline fuel cells and water electrolyzers, ie. stable to strong base and able to support current densities close to  $1 \text{ A cm}^{-2}$ . While details of the membranes are sketchy, some success can be reported.

The Italian Company, Acta spa [151], have reported performance data for a  $\text{H}_2/\text{O}_2$  fuel cell employing a membrane developed in collaboration with the University of Pisa and indicate the achievement of a current density of  $1 \text{ A cm}^{-2}$  although with a membrane IR drop probably approaching 250 mV. The Tokuyama Corp have been developing hydroxide conducting membranes with a lower resistance both by investigating new polymers and producing very thin membranes [152]. Several papers [153–156] report performance in an alkaline fuel cell and operation is possible with a power density of  $320 \text{ mW cm}^{-2}$  at a current density of  $0.8 \text{ A cm}^{-2}$ . Moreover, a hydrazine fuel cell based on these membranes achieves a power density  $620 \text{ mW cm}^{-2}$ , approaching the performance of acid membrane MEA cells. Fumatech in Germany [128] also market hydroxide conducting membranes for fuel cells but we are aware of no published performance data. CellEra Inc [157,158] are marketing a fuel cell stack (1.5 kW) with a MEA electrode configuration based on a novel hydrocarbon, hydroxide conducting membrane and non-precious metal catalysts; they claim low cost power generation at high current densities. ITM Power [159] also appear to have developed a hydroxide conducting membrane capable of supporting a high current density with a low IR drop. Using this membrane, Li and Pletcher [93] have reported a water electrolysis cell (not fully optimised) with a cell voltage of 2.10 V at a current density of  $1 \text{ A cm}^{-2}$ , see Fig. 6.

Hydrogenics market a zero gap, alkaline water electrolysis system under the tradename Hystat™ [14] based upon work by Vandenborre and coworkers [99,160–162]. It is, however, based on an inorganic ion exchange material, poly(antimonic acid) incorporated into a polysulfone organic binder. Unlike all the membranes discussed above, the membrane transports sodium ions, not hydroxide. When employing non-precious metal electrocatalysts,  $\text{NiCo}_2\text{O}_4$  and  $\text{NiCo}_2\text{S}_4$  deposited on perforated Ni plates as the electrodes, the performance is impressive. Cell operation above 373 K is possible while current densities as high as  $1.25 \text{ A cm}^{-2}$  can be achieved. At a current density of  $0.2 \text{ A cm}^{-2}$  the cell voltage is only 1.50 V. The technology is claimed to be both cheaper and more energy



**Fig. 6 – Cell voltage as a function of time over a 10 day period for an SPE cell with hydroxide conducting membrane.**

efficient than SPE cell based on Nafion™ membranes. These cells certainly demonstrate the possibilities for novel alkaline water electrolysis technology.

## 9. Conclusions and the future

We believe that the future of zero gap, alkaline water electrolyzers is highly promising. The low cost, non-precious metal electrocatalysts and hydrocarbon based membranes should lead to lower cost technology compared with zero gap, acid systems. The possibilities for low cost, energy efficiency water electrolyzers are excellent. The target should be a cell voltage  $<2\text{ V}$  at current densities  $>1\text{ A cm}^{-2}$  for cells operating below 373 K. At the present stage, we would assess the technology as follows:

- Low overpotential, stable hydrogen evolution catalysts are available.
- Stable oxygen evolution catalysts have also been developed but the overpotentials are much higher than desirable. In view of the very extensive research already focused on this problem, no major reduction in overpotential seems likely. Water electrolysis technology probably has to be live with this inefficiency.
- The next major improvements are likely to arise from improvements in hydroxide conducting membranes. While chemical stability has been improved, the structural changes needed to meet requirements of mechanical stability and high conductivity still seem to oppose one another. In addition, operation with a pure water environment would be highly desirable although cells with alkaline electrolyte environments may well have a role.
- Further optimisation of the design of zero gap alkaline water electrolyzers is essential. This includes studies to understand and improve the interface between membrane polymer and electrocatalysts and also materials and techniques for fabricating MEA type structures.

Work is in progress to decrease the energy consumption in other ways. The obvious route is to increase the temperature substantially. For example, cells with a highly concentrated KOH electrolyte and operating at up to 700 K, and at high pressure show much reduced overpotentials for oxygen evolution [163,164] and significant reduction in the cell voltage. Development to commercial technology will, however, require identification of novel, stable materials. Another approach for hydrogen generation technology is to replace the oxygen evolving anode by another anode reaction. Candidates that certainly decrease the thermodynamic energy input for hydrogen generation would be the oxidation of urea or methanol; indeed, reductions in cell voltage can be achieved [165] although the current densities for the reactions would need to be increased substantially. One can also question the 'green pedigree' of this approach since environmentally unfriendly products are also produced. For example, a cell where the anode reaction is the oxidation of urea would produce 0.33 mol of carbon dioxide for each mole of hydrogen (as well as the possibility of some oxides of nitrogen as minor products).

There is also current interest in the concept of reversible  $\text{O}_2/\text{H}_2$  fuel cells for energy storage [16]. This challenging concept envisages the generation of hydrogen and oxygen during charge (or the storage of energy) and the recombination back to water during discharge (or the release of stored energy) in a single cell. Despite an extensive literature on catalysts [17,166], at present, the energy efficiency is very poor, certainly  $<40\%$ . Significant improvements are only probable when high performance alkaline water electrolyzers have been achieved.

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