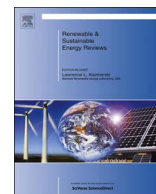




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## Process intensification: An electrochemical perspective

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## ABSTRACT

This paper provides a review of a range of process intensification methods which have been applied to electrochemical processes and reactions. The electrochemical reactions include those in electrolyzers where gas evolution occurs, in metal deposition reactions and reactions occurring in fuel cells and batteries. The process intensification methods include the use of centrifugal force fields, ultrasonics, rotating electrodes and rotating cells which operate with and without the application of magnetic fields. Such devices can be used in principle to carry out electrolysis without the application of an external potential or current. Other methods considered include the use of light. The area of magnetic field induced fluid flow is also discussed which has applications in lab on a chip technologies. The area of process intensification has largely focused a lot on hydrogen generation as a means of providing a clean, sustainable fuel.

## 1. Introduction

Process intensification (PI) may be seen as a generic method or series of tools that seeks to improve process performance in terms of better energy efficiency, lower product or system cost, and better sustainability. As such the application of PI looks to exploit different equipment (reactors, separators, contactors) and apply different methods, such as alternative fluids and phases, extreme operating conditions, multi-functional devices and energy types such as centrifugal fields, ultrasound, solar, light, microwaves, electric fields, plasmas and magnetic fields [1]. Process intensification has been applied to a wide range of reaction systems involving chemical, catalysis and mass transport processes and to a lesser extent electrochemical processes.

Electrochemistry is concerned with the transfer of charge, by the movement of ions, in a liquid or solid (or gaseous) phase through which electrochemical transformation of species can be achieved (Fig. 1). Electrochemistry can be used to synthesise materials and chemicals, to generate power and to analyse and detect compounds and components. The applications of electrochemistry are quite diverse and span over a wide range of industries. Improvements in performance of electrochemical technology are targeted at reduced energy consumption, or higher power output (in the case of energy storage devices), increased reaction rates through higher current densities which result in smaller cells and lower cost or the ability to use renewable energy such as wind and solar energy or even biomass or waste in for example bio-electrochemical fuel cells [2].

This article provides a review of strategies that have been applied to

improve electrochemical technologies (see Table 1) by applying PI tools, such as centrifugal fields, magnetic fields, light and ultrasound. The review provides examples of where PI has been used advantageously in technologies for synthesis (hydrogen, oxygen, chlorine, organic synthesis, batteries and fuels) and considers the potentials of the approach as well as related limitations.

## 2. Electrochemical technologies

Electrochemistry is concerned with the transfer of charge, by the movement of ions, in a liquid or solid (or gaseous) phase through which electrochemical transformation of species can be achieved. Electrochemistry can be used to synthesise materials and chemicals, to generate power and to analyse and detect compounds and components. The applications of electrochemistry are quite diverse and span over a wide range of industries, including; energy storage and power generation, synthesis of chemicals and materials, extraction and production of metals, recycling, water purification and effluent treatment, corrosion protection, analysis, sensors and monitors, metal and materials finishing and processing, and semiconductor technology including photo-electrochemistry. Electrochemistry is used in the finishing of many components through the deposition of coatings (metallic, polymer) and through anodising to produce surface oxide films. Electrophoretic painting is used widely in the motor industry for bodywork protection. Other applications are in electropolishing and in electrochemical cleaning, pickling and stripping [3].

An important area for electrochemistry is in sustainable, clean and

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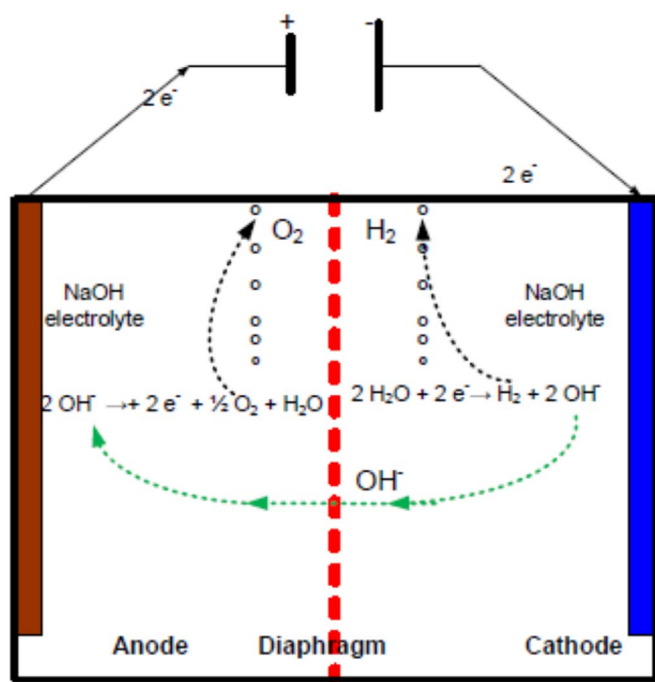


Fig. 1. Processes in an electrochemical cell.

renewable energy [4]. Renewable energy can be stored in batteries, capacitors or converted into hydrogen for later use. Renewable energy may be used to synthesise chemicals, e.g. from carbon dioxide electrochemical reduction. Solar energy can be used to generate chemicals such as hydrogen and oxygen by photo-electrolysis or in electrosynthesis of chemicals.

Energy storage and generation through the application of batteries, capacitors and fuel cells have a common feature; an electrochemical cell featuring two electrodes connected via a conducting electrolyte. The generation of electrical energy within a battery or fuel cell is caused by two “redox” reactions (with a negative free energy) which occur spontaneously or in a capacitor from the liberation of an accumulated charge. Fuel cells are devices for generating electrical power by the continuous supply of a fuel to one electrode and an oxidant to the other electrode. There are a variety of these devices which operate at low or high temperatures. The electrodes in fuel cells are different to those in batteries as they must generally be permeable to gases. In low temperature cells catalytic gas diffusion electrodes are therefore used which are typically a composite structure of electrocatalyst, carbon, hydrophobic binder and a coating.

Electrochemical synthesis is used for production of both organic

and inorganic chemicals. The two largest industries (in terms of tonnage) are for the combined chlorine and caustic soda (NaOH) production (chlor-alkali) and aluminium electrowinning. These two processes use radically different cell technology, aluminium production being based on molten salt electrolysis at temperatures around 1000 °C, whilst the chlor-alkali industry is based on the electrolysis of aqueous brine solutions at low temperatures around 60 °C. Other inorganic electrochemical processes include the production of hydrogen by water electrolysis, molten salt electrowinning of sodium, lithium and magnesium and electrowinning from aqueous electrolyte of copper, zinc and nickel and a range of compounds such as ozone, hydrogen peroxide, sodium hypochlorite, potassium permanganate, persulphates, etc. [5,6].

The electrosynthesis of organic chemicals is mainly located in the fine chemical industries where the advantages of this technique have seen somewhere in the region of a hundred or so industrial processes developed. Electrochemical technology is used in relatively few bulk organic chemical syntheses due to the relatively large equipment cost in relation to product value and energy input. In addition the strong presence of heterogeneous catalysis makes competition difficult; especially with a fluctuating electrical energy market. An important exception to this is the production of adiponitrile from acrylonitrile (an intermediate in the production of nylon) [3].

### 2.1. Improvement in electrochemical technologies

In the electrochemical industries mentioned above a range of strategies have been explored to gain improved performance and better energy efficiencies. These generally introduce methods by which electrocatalysis can be improved by using more active or higher surface area, catalysts and/or by increasing mass transport to electrode surfaces so as to increase reaction rates at lower electrode overpotentials. In the latter case improved mass transport can be achieved by introducing enhanced turbulence through the use for example of turbulence promoters, use of high surface area electrodes or by movement of the electrode structure. Enhanced performance in electrochemical cells can also be realised by modifying conditions of operation, e.g. temperature and pressure, by exploring alternative cell reactions and by using alternative electrolytes and electrodes.

#### 2.1.1. Electrochemical reaction rate, voltage and efficiency

The rate at which a species reacts or is produced is defined by Faraday's Law and can be written as [4]:

$$N = I/(nF) \text{ (mol s}^{-1}\text{)} \quad (1)$$

Thus for example, in the case of hydrogen formation, Faraday's Law tells us that 1.0 mol of hydrogen gas (22.4 dm<sup>3</sup>, at STP) is produced from  $2 \times 96485 \text{ C (A s)}$  of charge.

**Table 1**  
Impact of Process intensification methods in Electrochemical processes Y – positive effect.

Reaction	Process Intensification Parameter							
	Centrifugal force/ High G	Ultrasound	Solar/light	Electric field	Magnetic field	Magnetic material	Moving electrodes	Rotating flow
Electrochemical gas evolution, e.g. H <sub>2</sub> , O <sub>2</sub> , Cl <sub>2</sub> ,	Y	Y	Y		Y	Y	Y	Y
Metal deposition		Y			Y		Y	
Fuel cells	Y		Y			Y	Y	
Batteries					Y	Y	Y	
Electrolysis- organic and inorganic synthesis,	Y	Y			Y		Y	
Environmental remediation and effluent treatment		Y	Y				Y	
Gas/liquid reactions	Y	Y			Y		Y	Y
Fluid motion				Y	Y			

In electrochemical technology the rate is generally normalised in terms of the cross-sectional area of the electrodes,  $A$ , using current density  $i = I/A$ . Thus the production capacity,  $J$ , is conveniently expressed as [4]:

$$J = i \times CE / (nF) \text{ mol m}^{-2}\text{s}^{-1} \quad (2)$$

Where  $CE$  is the current efficiency (expressed as a fraction) or the yield of a process based on the charge passed and can be defined as:

$$CE = \frac{\text{charge consumed in forming product}}{\text{total charge consumed}} \quad (3)$$

Current efficiencies less than 1.0 arise because other reactions at an electrode can also consume charge. For example, in water electrolysis in which hydrogen and oxygen are formed, reduction of dissolved oxygen at the cathode and hydrogen oxidation (because of gas diffusion through the membrane) and ozone production at the anode can occur. These reactions can reduce the amount of hydrogen and oxygen produced and thus cause current efficiencies  $< 100\%$ .

In practical operation high current densities are targeted to maximise the production rate although this must be balanced by the effect they have on the voltage required and the energy used for operation.

The electrical energy consumption of an electrolyser is determined by the cell voltage  $E_c$  and is given by [4]:

$$\text{Energy consumption} = nF E_c / CE \text{ (Ws/mole)} \quad (4)$$

Where  $E_c$  is the cell voltage.

The energy consumption is minimised by operating with a current efficiency as close to 100% as possible and with the lowest practical cell voltage. The selection of the electrodes and the separator and the operating parameters are significant factors in this.

In the case of fuel cells (or batteries) Eq. (4) above is modified to give a measure of the energy generated (rather than consumed and hence  $CE$  is in the numerator) in kWh for a unit mass of fuel (or oxidant) consumed.

$$\text{Energy produced} = nF \times E_c \times CE / [3600 \times M] \text{ (kWh/kg)} \quad (5)$$

### 2.1.2. Cell voltage

Cell voltage is determined from thermodynamics of the reactions, the electrochemical kinetics, transport processes and the cell design. The various components which make up the cell voltage in an electrolyser are illustrated in Fig. 2, and the cell voltage can be calculated from [4]:

$$E_{\text{cell}} = \Delta E_e - |\eta_{c, \text{activation}}| - |\eta_{a, \text{activation}}| - IR \quad (6)$$

Where  $\Delta E_e$  is the sum of the equilibrium potentials of cathode and anode reactions, i.e. the reversible cell voltage,  $\Delta E_{e, a}$  and  $c$  are the overpotentials at the cathode and the anode and  $IR_{\text{cell}}$  are the Ohmic voltage losses in the electrolytes, the cell separator, electrodes and in the connections from the power supply to the electrodes. Because the electrolyser requires energy to operate and the Gibbs free energy change is positive (i.e.  $E_c$  is negative) all terms in Eq. (14) are negative, although often in the literature the cell voltage is expressed as a positive value.

Activation losses are caused by sluggish electrode kinetics and are the result of complex, surface electrochemical reactions. In the case of most cells operating at practical, relatively high, overpotentials ( $\eta_{\text{act}} > 50\text{--}100$  mV), a Tafel type relationships can approximate the voltage contribution due to activation polarisation [4]:

$$\eta_{\text{act}} = \frac{RT}{\alpha nF} \ln\left(\frac{i}{i_0}\right) \quad (7)$$

where,  $\alpha$ , is the charge transfer coefficient,  $i_0$  is the exchange current density.

This relationship does not consider the influence of mass transport

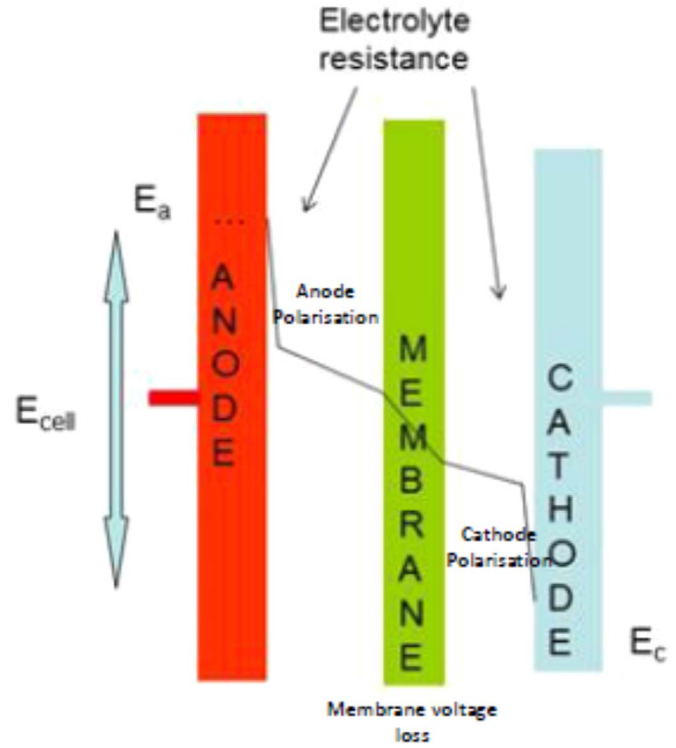


Fig. 2. Cell voltage contributions in electrochemical cells.

and thus concentration changes on the activation polarisation. Where mass transport has an influence this affects the exchange current density which is in fact a function of the reacting species concentration at the electrode surface.

Ohmic polarisation occurs because of the resistance to the flow of ions in the electrolyte and to the flow of electrons through the electrode and any contacts between cell components. The associated voltage contribution is given by [4]:

$$V = IR = I(R_{\text{electronic}} + R_{\text{ionic}} + R_{\text{contact}}) \quad (8)$$

where  $R$  is the total cell resistance, which includes electronic, ionic, and contact resistances.

The resistance of the electrolyte and associated cell separator frequently constitutes a major component of the  $IR$  loss in a cell. The Ohmic resistance is defined by the electrolyte resistivity,  $\rho$  (ohm m), or alternatively by the electrolyte conductivity,  $\kappa$  (S/m) as

$$R = \rho d/A = d/(\kappa A) \quad (9)$$

Where,  $d$ , is the inter-electrode gap.

The voltage loss is thus expressed as

$$V = i\rho d = i d/\kappa \quad (10)$$

The electrolyte conductivity should be high, using appropriate conducting electrolytes, although this must not prove detrimental to the stability of the electrodes and the separator and to the performance of the reactions. The electrode design and material should also facilitate efficient gas release from its surface, in for example the electrolysis of water to hydrogen (and oxygen), to ensure that the  $IR$  drop in the electrolyte and the "bubble polarisation" is low. The dominant Ohmic losses through the electrolyte are reduced by decreasing the electrode separation and increasing the ionic conductivity of the electrolyte. The resistivity is a function of the cell design, material choice, manufacturing technique and temperature.

To be consistent with the previous terminology of using current density, the Ohmic resistance is often normalised by the cross-sectional cell area ( $A$ ) is an Area Specific Resistance (ASR) which has units of  $\Omega \text{ cm}^2$ . Thus the voltage loss is given by:

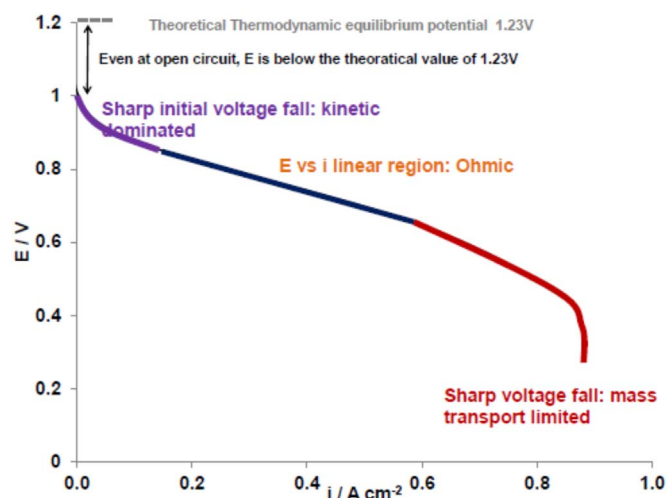


Fig. 3. Voltage and power density behaviour of fuel cells.

$$V = i \times ASR \quad (11)$$

In the case of fuel cells the voltage falls as the current density increases due to the combined effect of all polarisations on the cell voltage includes the contribution of the anode and cathode potentials and Ohmic polarisation. The extent of the electrode polarisation losses in a fuel cell are illustrated in Fig. 3. The net result of current flow in a fuel cell is to increase the anode potential and to decrease the cathode potential, therefore decreasing the cell voltage.

The cell voltage for a fuel cell is written as for an electrolyser:

$$E_{\text{cell}} = \Delta E_e - |\eta_{\text{c, activation}}| - |\eta_{\text{a, activation}}| - IR \quad (12)$$

This expression is similar to an electrolyser except in the latter, the magnitude of the voltages increase with current as the polarisation and Ohmic resistance contributions increase and the efficiency falls.

Efficiency is essentially an expression or measure of an electrolyser or fuel cell voltage point of operation relative to the thermodynamic potential. So for example for an electrolyser efficiency can be given by:

$$\eta_{\text{electrochem}} = E_e / E_{\text{cell}} \quad (13)$$

where,  $E_{\text{cell}}$  is the operating voltage of the electrolyser at a given current density  $i$  and operating temperature  $T$ , and  $E_e$  is equilibrium Nernst potential at the same temperature.

For a fuel cell the efficiency is the inverse of Eq. (13), as the cell voltage will always be lower than the equilibrium value under practical conditions.

## 2.2. Gas evolving electrodes

In many of the cells used for electrochemical synthesis a two phase gas, liquid mixture is produced which impacts on energy consumption in terms of increased Ohmic resistance in the electrolyte. This is largely due to bubbles which hinder the movement of ionic species (i.e. reduce the effective ionic conductivity) or which block the electrode(s) surface, and thereby reduce the effective electrode reaction sites, by clinging to the electrode or forming a bubble curtain (see Fig. 4). As a consequence of this effect the voltage required for electrolysis as defined by Eq. (6) may increase:

One of the oldest and most important electrochemical process is the production of chlorine and caustic soda (NaOH) from brine which also produces a third product; hydrogen. This process or cell reaction is typical of many electrochemical reactions as it involves the formation of two-phase gas liquid electrolyte systems through bubble generation from one (or two) electrode surfaces. Chlor-alkali production is the largest scale industrial electrosynthesis; a rate of  $3.5 \sim 4.0 \times 10^7$  t  $\text{Cl}_2$  per year world-wide [33]. The progress in chlor-alkali technology has

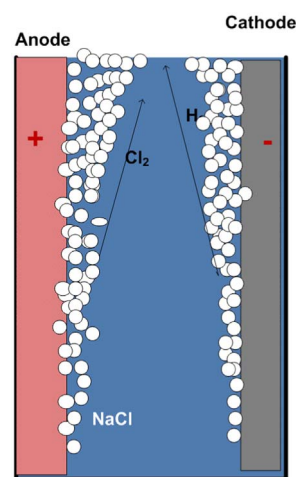


Fig. 4. Bubble curtain effect at gas evolving electrodes.

been reviewed extensively in the literature [e.g. 7,8]. Under typical operating conditions the reversible potentials are, at the anode 1.247 V (versus reversible hydrogen electrode, RHE), at the cathode  $-0.797$  V (vs. RHE), giving a total reversible cell voltage of 2.23 V. At the current densities used, i.e.,  $1\text{--}5 \text{ kA m}^{-2}$ , one of the major issues confronting the chlor-alkali industry is the high power consumption, about  $10^8$  MW h of electricity per year. It was estimated that the power consumption accounts for over 50% of the operating costs [9].

Significant improvement of the electrolytic process in this aspect, i.e. reduction in cell voltage, would be beneficial, both economically and environmentally. Chlor-alkali electrolysis involves the generation of gases at both of the electrodes, e.g., chlorine evolution at the anode and hydrogen evolution at the cathode. This can introduce a relatively high resistance of the cell due to severe gas blanketing of the electrodes and the membrane and poor conductivity of the bubble-filled electrolytes. Both effects incur significant overvoltage, e.g. about 0.4 V at a current density of  $3 \text{ kA m}^{-2}$  in ICI electrolyzers (FM21 units). Therefore, it is important to try and ensure efficient gas disengagement from the electrolyte, the electrodes and any intervening diaphragm/membrane, in the operation of chlor-alkali cells.

Gas disengagement can be achieved in various ways, such as pumping electrolyte through the electrochemical cell or using moving electrodes, etc. However, such methods have a limited effect on enhancing mass transfer and eliminating bubble effects. For example, the rotating cylinder electrode may be used [10], but enhancement in mass transfer to a rotating cylinder electrode depends to a large extent upon micro turbulence at the electrode surface and is at the expense of high shear losses.

In electrolysis reactions which involve gas bubble formation, acceleration of the detachment of bubbles from electrolytic system is beneficial to enhance water electrolysis, if it can achieve more effective disengagement of bubbles from electrode, and also possibly the membrane surface, so as to decrease reaction overpotential and more effective spill-over of bubbles from the electrolyte and rapid removal of bubbles from electrode surface. The common approach to improve gas bubble disengagement is to use flow or turbulence promoters but, Ohmic voltage losses and overpotentials can only be reduced to a limited extent, due to practical limitations. These limitations include excessive pressure losses during flow and low conversions of reactants per pass through the cells. Consequently this has increased interest in the use of external fields in electrolysis. One option for intensification is to design equipment wherein the electrolyte is subjected to a centrifugal force to promote good mass transport within the cell and the separation of gas bubbles from the electrodes, the electrolytes and the membrane. This approach is an attractive strategy in the chemical industry and was pioneered in ICI during the late 1970's [11].



**Table 2**

Direct impact of process intensification methods on rate processes.

	Centrifugal force/High G	Ultrasound	Solar/light	Magnetic field/material	Moving electrodes	Rotating flow
Mass transport	✓	✓		✓	✓	✓
Kinetics		✓	✓	✓		
Energy input	✓	✓	✓	✓		

### 3. Intensification by external fields

The use of process intensification strategies is generally targeted at trying to radically increase mass transport rates at electrode surface or to increase interfacial mass transfer between fluid phases. Additionally certain methods such as ultrasonics have the ability to modify kinetics of reaction. In either case one important character is the resulting reduction in the direct electrical energy input (see Table 2). In the following sections the applications of PI strategies to a range of electrochemical systems is described.

#### 3.1. Rotating electrodes and cells

The use of rotation of devices has been a classic method to attempt to intensify system operation in a range of mass transport controlled processes. In line with this the use of rotation in electrochemical cells has been applied for decades in a number of applications. This includes metal depositions, gas evolution, two phase electrolysis, electro-flotation etc., as well as their use in electro-analysis using rotating disc and rotating ring disc electrodes [12]. Other routes to intensify electrochemical processes include the use of high surface area electrodes, moving particulate and fluidised bed electrodes, membrane reactors and modification of operating conditions, e.g. high temperature to improve thermodynamic efficiencies by supplying more energy as heat and less as electrical energy as, for example, proposed for high temperature steam electrolysis to produce hydrogen [13].

##### 3.1.1. Rotating electrodes

In metal recovery applications rotating cathode cells have been employed in order to enhance mass transfer from the bulk to the electrode surface and also to remove the resulting deposited metal powders from the cathode. Two systems in particular have been developed (see Fig. 5) based on rotating cylinders and rotating discs or the pump cell [14,15]. In such systems by using a static anode and a rotating disc cathode, the narrow spacing between the electrodes allows the entrance of the effluent. Another design employed rotating rod cathodes in between inner and outer anodes. In addition to metal recovery, it is also possible to use the anode for simultaneous destruction of cyanides if necessary [16]. The mass transport behaviour of such systems has been studied using both experimental and theoretical methods [14,17].

Another rotating disc electrolyser uses a system where both electrodes are rotating as two parallel discs, with axial inlet of electrolyte. One of the disc electrodes is provided with a central hole for the electrolyte inlet [18]; the electrodes are electrically insulated and fixed to a common axis, around which they rotate (Fig. 5).

In attempts to further improve performance and efficiency, three dimensional, rotating electrodes have been employed [19]. One application was in the treatment of metal complexes in wastewater from electroplating industries. In this work, the destruction of Cu, Ni and Cr complexes from electroplating by electro-oxidation was achieved using a Hige electrochemical reactor with rotating mesh-disc electrodes. The rotating electrodes consisted of four titanium mesh-discs as cathodes and three titanium-based lead dioxide mesh-discs as anodes. The rotation of electrodes was shown to enhance the mass transfer of electrochemical process [20]. Gao et al. [21], reported the use of a Hige electrochemical reactor to treat phenol wastewater,

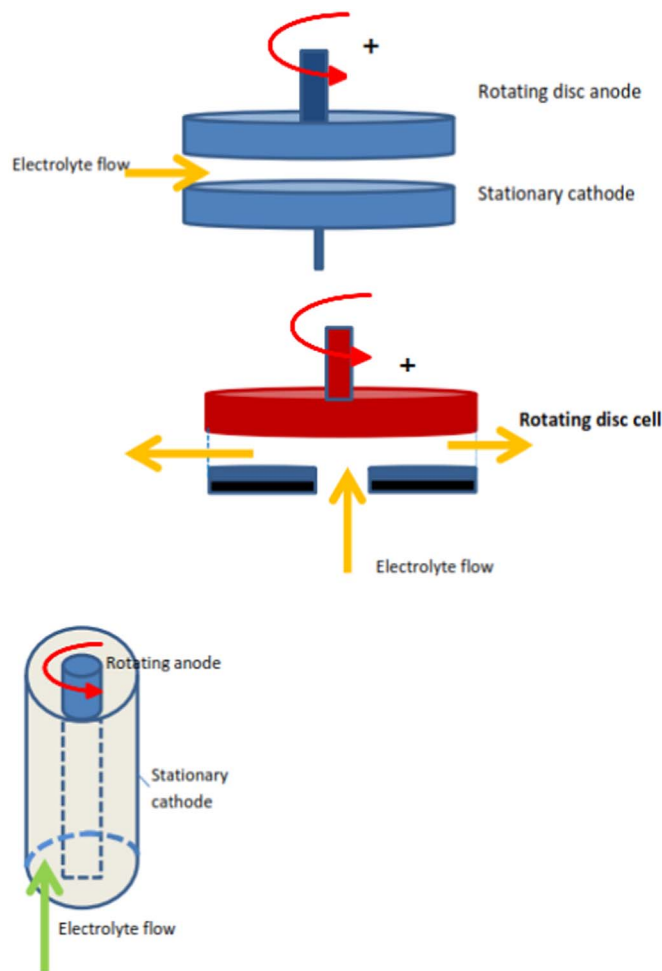


Fig. 5. rotating cylinder and rotating disc electrolysers.

the COD removal efficiency was about twice that achieved in the normal gravity field.

Zhong et al. [22] investigated the de-colorization of reactive brilliant orange X-GN by a rotating electrochemical disc cell. Half of the disc electrodes, which consisted of granular activated carbon, filled between the anodes (graphite) and the cathodes (copper), were exposed to the air to accelerate oxygen mass transport from air to liquid.

As well as rotating mesh discs, rotating three dimensional cylinder electrodes have been studied, e.g. the mass transfer behaviour at rotating cylinder electrodes of woven-wire meshes using the reduction of ferricyanide as the test reaction. The mass-transfer enhancement factor for three-dimensional electrodes is described through the use of dimensional group correlation of Sherwood number and Reynolds number [23].

Kreysa [24,25] investigated the behaviour of a rotating packed bed cell with an external radial flow of electrolyte superimposed on the electrolyte flow induced by the electrode movement. A dependence of the Sherwood number on two Reynolds numbers, one convective and the other rotational, to the power 0.58 was reported. It was found that

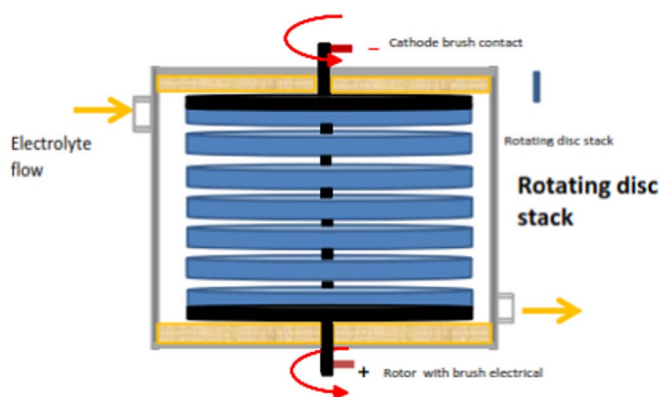


Fig. 6. Rotating stack of disc electrodes.

the mass-transfer coefficients of the three dimensional rotating electrodes were about three times higher than those obtained with smooth rotating cylinder electrodes [26,27].

The concept of using rotating electrode devices has been applied in a number of synthesis application for example in hypochlorite production where a patent was filed by Greaves [28]. In this a rotating disc stack was described for the production of sodium hypochlorite from the electrolysis of sea water. The system was comprised of a set of rotating bipolar connected platinised titanium discs rotated about a central axis through which the electrolyte solution flowed (Fig. 6). Advantages of the device include reduction in insoluble magnesium hydroxide deposits on the electrode surface and improved mass transport conditions.

### 3.1.2. Centrifugal (supergravity) field

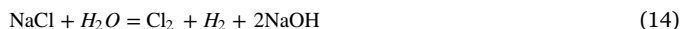
Process intensification is in principle particularly attractive for electrochemical processes that are, typically, multiphase systems. The practical application of process intensification in reaction systems requires the introduction of fluid dynamic conditions which stimulate high mass transfer rates that with given intrinsic kinetics, do not limit the overall rate. Although several methods can be used such as pulsed flow, ultrasonics, rotational or Dean flow, etc, the centrifugal field is perhaps one most widely applied to processes involving two phases [29–31]. Generally speaking, in electrolytic process this can result in a substantial reduction in cell voltage at a given current density, particularly with large current densities. Systems where the method could be successfully used include, liquid-liquid dispersions and gas liquid dispersions where interfacial mass transport may be rate limiting, in for example hydrogen peroxide formation from the reduction of oxygen, and where electro-generated bubbles adhere to the electrodes. In addition, with the so-called zero-gap designs, there may be also issues related to bubble adhering to the surfaces of membranes. Furthermore they help address issues with high gas volume fraction accumulation in the electrolyte, which reduce ionic conductivity and where relatively large electrode spacing are used to offset the effect of bubble induced resistance.

Hydrogen energy systems are considered now as promising in the effort to overcome environmental problems and generation of hydrogen by water electrolysis offers one solution to this problem through its clean production of the gas. Thomson as early as 1929 was one of the first to identify exploiting centrifugal acceleration fields for facilitating gas disengagement for water electrolysis and thereby improve performance [32]. Even now the practical application of this method has never materialised much beyond laboratory demonstrations. This is despite the fact that to enable practical electrolysis plant costs, industrial electrolyzers typically operated at high current density ( $1000\text{ s A/m}^2$ ) incurring significant voltage penalties above the thermodynamic decomposition voltage; due to high overpotentials, especially for the oxygen evolution and IR voltages.

In practice many electrochemical systems can benefit from process intensification and include cells where gas evolution occurs at one electrode, which may be the counter electrode;

- in metal depositions with oxygen evolution,
- inorganic synthesis with hydrogen as the byproduct at the counter electrode, e.g. permanganate from manganate
- organic electrochemical reduction or oxidation syntheses with oxygen or hydrogen as by-product
- synthesis involving processes in two phase liquid-liquid dispersions or emulsions, e.g. adiponitrile synthesis by reduction of acrylonitrile,, which also involves an oxygen evolving counter electrode reaction and hydrogen as by-product from the reduction
- reactions in which reactants are in the gas phase such as oxygen (for peroxide formation), carbon dioxide, chlorine
- fuel cell reactions in which say carbon dioxide is formed from oxidation of an organic fuel

As noted above chlorine production has been studied in the context of process intensification. This is because the cell reactions involve two gas evolving reactions, for  $\text{Cl}_2$  and  $\text{H}_2$ :



One of the earliest reports of process intensification was for a rotating chlor-alkali cell in a patent by Hoover [33]. The concept was further extended by Ramshaw [11] who also used a PEM chlor-alkali cell.

In general, the beneficial effects of centrifugal fields result from differences in forces applied to fluids of different densities. When a centrifugal field is applied to a multi-phase system, the light phase, e.g. gas, will flow inward, whereas the centrifugal effect will tend to sweep the denser fluid outward. In a cell this can provide a rapid and efficient removal of the electrolytic gas from the inter-electrode gap. The inter-phase buoyancy force determines the fluid dynamics of multiphase systems and because this force is large in a centrifugal field, droplets and/or bubbles will be small and the inter-phase slip velocity will be high [11]. Moreover, bubbles disengagement from the electrodes, electrolytes, membranes, and the inter-electrode area would be greatly facilitated in a centrifugal field; greatly reducing gas blanketing, thereby making significant reductions in the cell voltage. The idea was demonstrated by preliminary work at ICI with a rotating chlor-alkali membrane cell [11]. The rotating unit comprised of two opposing spinning disc planar electrodes which were coated with an appropriate electro-catalysis. When operated under similar conditions to those encountered in a commercial ICI cell (FM21), very significant overall voltage savings were achieved in centrifugal fields. In comparison to the standard ICI FM21 operating at around as  $3.17\text{ V}$  cell voltage at  $3.0\text{ kA m}^{-2}$ , it was found that the rotating unit when operated at accelerations up to  $200g$  (about  $900\text{ rpm}$ ) gave very significant energy savings. At  $5.0\text{ kA m}^{-2}$  the voltage reductions were even greater.

It should be noted in this system that the energy needed to rotate the cell and overcome windage, friction etc., will be quite small compared to that which could be saved for electrolysis industrial application. For example, a  $100\text{ kA}$  cell operating with a bubble overvoltage of  $0.3\text{ V}$  has a potential energy saving of approximately  $30\text{ kW}$  whereas the equipment rotor ( $1\text{ m}$  long  $\times$   $0.5\text{ m}$  diameter) will require approximately  $2\text{ kW}$  to rotate at around  $700\text{ rpm}$  [11].

Cheng et al. [34] investigated chlor-alkali electrolysis in a conventional laboratory centrifuge using acidified brine and at temperatures up to  $353\text{ K}$ . The relationship between cell performance and the relative acceleration was evaluated using  $\text{RuO}_2\text{--TiO/Ti}$  mesh and  $\text{Pt/Ti}$  mesh electrodes and very significant cell voltage reductions were generated with accelerations up to  $190g$ , e.g. a reduction of  $0.6\text{ V}$  was observed at a current density of  $6.0\text{ kA m}^{-2}$ . In addition, the electrode mass transfer coefficient increased from  $1.3 \times 10^{-5}\text{ ms}^{-1}$  to  $3.9 \times 10^{-4}\text{ ms}^{-1}$ . Cheng et al. [35] also investigated water electrolysis and

again showed that centrifugal fields provided a powerful means for improving the electrolytic process, with cell voltage reductions of some 0.36 V at  $3.0 \text{ kA m}^{-2}$ , when nickel foam electrodes were used with concentrated potassium hydroxide solutions.

The relationship between cell voltage of a water electrolysis under super gravity field ( $E_G$ ) and the applied G acceleration has been expressed in the following empirical equation [36]:

$$E_G = E_{\text{cell}} - K \log(G) \quad (15)$$

where K is a constant at a specific current density and  $E_{\text{cell}}$  is cell voltage under normal gravity conditions.

The effect of the G acceleration is such that the higher current density for water electrolysis applied, the larger the effect of super gravity field on cell voltage reduction, i.e. the value of K increases with current density. The maximum percent of energy saving is up to around 17% [36]. Cheng also developed a mathematical model to explain the experimental observations for hydrogen electrolyzers, chlor alkali cells and direct methanol fuel cells [37]. The model took into account the effect of relative acceleration rate on the mass transfer coefficients, the gas fraction, the cell voltage, and cell voltage reduction. Comparison between the experimental results and the modelling data showed satisfactory agreement (Fig. 7).

It is well described that cell voltage reduction originates from rapid disengagement of bubbles from electrode surface and electrolyte. Bubble formation on electrode surfaces and the effects of centrifugal field have been studied by several researchers during water electrolysis [38]. It was observed that many bubbles, with diameter of about 200  $\mu\text{m}$ , were attached to the electrodes under a normal gravity field, but much smaller bubbles were seen under supergravity. Overall the supergravity field promotes the disengagement of bubbles and decreases bubble coverage on electrode surface with resultant reduction in electrode overpotential and Ohmic voltage drop. From theoretical predictions based on nucleation theory the critical volume of bubbles was only 0.094 times, and the buoyancy force was 18.8 times greater under super gravity field ( $G = 200$ ), compared to those under normal gravity conditions [38]. Thus a larger buoyancy force and smaller bubble volume under super gravity field are thus seen as favourable for rapid separation of bubbles from electrode surfaces.

The above studies, although clearly identified that enhanced acceleration under supergravity applied to an electrolysis can result in major improvements in energy efficiency, most studies were not conducted in cells that would be readily scale-able to industrial electrolyzers; often

with electrodes immersed in a pool of electrolyte and rotated together inside a centrifuge. More recently Lao et al. [39] tested a single cell disc rotary electrolyser over a range of current density, centrifugal acceleration, electrolyte concentration, temperature, and electrode geometry. The rotary electrolyser cell voltage achieved (with a 7.7 M KOH solution, at 348 K) at an acceleration of about 16g, equivalent to a rotational speed of 500 rpm in the system used, was some 0.25–0.5 V, less than the equivalent static cell under similar operating conditions. The cell voltages reported were with Ni mesh based electrodes, without an electrode catalytic coating, and were comparable with those for typical industrial alkaline pressurised electrolyzers. At a higher acceleration of 41G, the rotary cell's current density can be as high as  $13.5 \text{ kA m}^{-2}$  without gas bubble blinding the electrodes.

### 3.1.3. Electrochemical power sources

There have been a limited number of studies of rotating electrodes and cells to electrochemical power sources, such as batteries and fuel cells. Ramshaw applied the rotating cell/electrode to a system related to fuel cell electrode operation [11]. This system applied the use of supergravity in a rotating cell using aqueous KOH solution and an oxygen reduction electrode based on silver coated carbon fibres. The system used an air gas feed essentially sparged into the cathode chamber and demonstrated a reduction in potential of between 0.95 V and 0.8 V at current densities of  $0.5\text{--}1.5 \text{ kA m}^{-2}$ , compared with a nitrogen sparged system where the reaction would have been hydrogen evolution. These voltage savings compared favourably with the thermodynamic voltage saving of around 1.2 V and with voltages achieved with practical ORR depolarised cathodes. The performance of the same stationary cell with a flowing electrode produced mass transport limiting current densities of around  $0.1 \text{ kA m}^{-2}$ , demonstrating the good mass transport conditions in the rotating cell.

This type of gas sparged operation has applications where electrochemical cells normally use hydrogen evolution as the counter electrode reaction but by replacing this with the ORR a theoretical voltage saving of some 1.2 V can be achieved (Fig. 8). This concept has been applied industrially in commercial chlor alkali cells operated by Bayer [40]. It could also be applied in other applications involving reaction of gases which have low solubility in electrolytes, e.g. carbon dioxide. It also can be applied in fuel cells such as alkaline fuel cells using hydrogen and oxygen (air) or hydrogen peroxide, and in fuel cells using inorganic chemicals, e.g. chlorine, and organic chemicals using for example formic acid, ethers and alcohols. However there have been limited reports of applications of this type other than that of Cheng et al. on direct methanol fuel cells (DMFC) who operated and evaluated it in a centrifugal field [41]. It was observed that methanol oxidation reaction was significantly intensified in a centrifugal field. The application of centrifugal fields greatly enhanced mass transfer and accelerated gas bubble disengagement from the electrode surfaces, the electrolytes and the membrane during the methanol oxidation. The reduction in the anode potential up to 500 mV at  $300 \text{ mA/cm}^2$  was achieved at a relative acceleration rate of 190g and  $80^\circ\text{C}$ , compared with a static cell. Increases of methanol concentration and operating temperature contributed to great increase in methanol oxidation rate. These beneficial effects were improved further in a centrifugal field, compared to in a gravitational field. The MEA consisted of anode of a Pt/Ru coated Ti minimesh or carbon cloth and the anode a Pt/C coated carbon cloth and a central Nafion membrane. A beneficial effect of the centrifugal field on the direct methanol fuel cell performance was observed (Fig. 9). However it is important in the design that to guarantee efficient oxygen supply to the cathode under the centrifugal acceleration conditions and thus to increase power output by this particular approach.

A rotating PEMFC configuration has been described in a US patent [42]. In the design, hydrogen enters a central rotating shaft and is distributed evenly to a series of PEMFCs located at right angles onto the shaft. The cell has the air cathode exposed to the atmosphere and

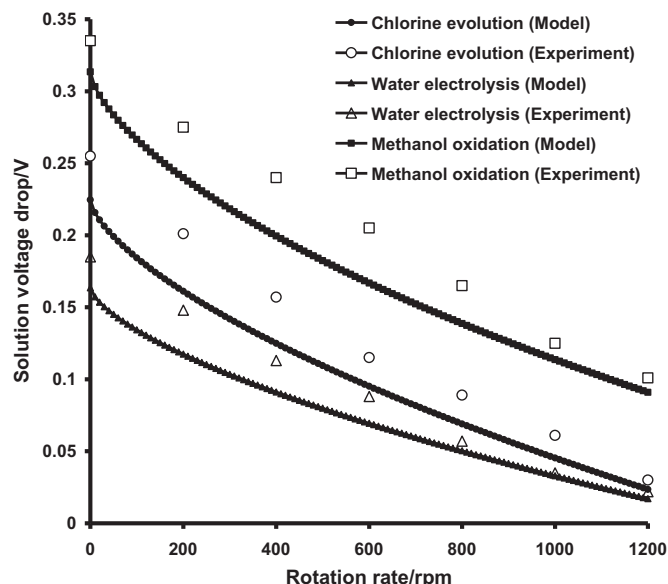


Fig. 7. Effect of centrifugal fields on electrolyte solution voltage drop for gas evolving reaction.

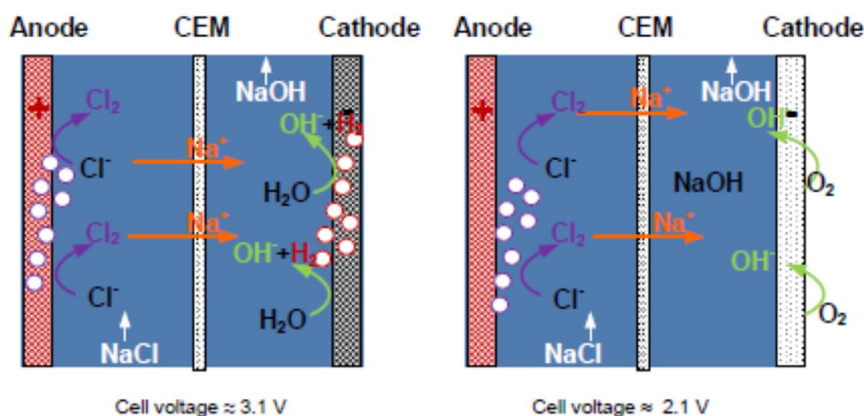


Fig. 8. Oxygen reduction reaction applied to chlorine cells.

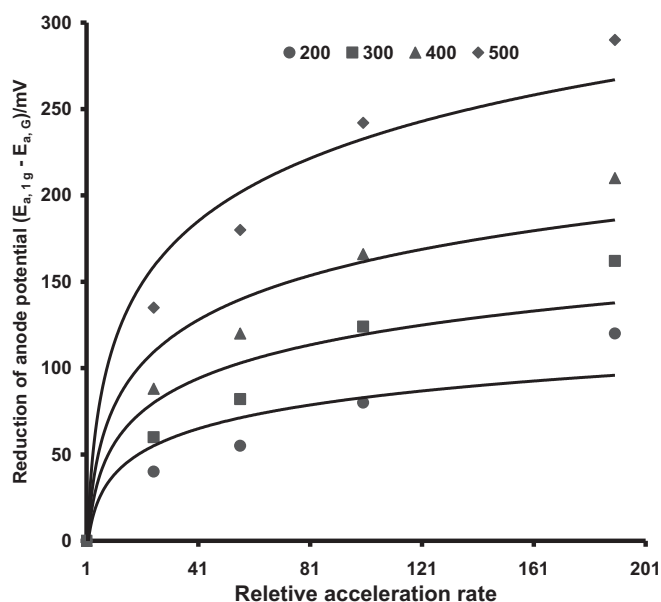


Fig. 9. The effect of a centrifugal field on methanol oxidation fuel cell anode potential against relative acceleration rate plots for  $\text{CH}_3\text{OH}$  oxidation in the rotary cell. Current density: shown in the figure ( $\text{mA cm}^{-2}$ ). Anode: Pt-Ru/Ti mini-mesh. Cathode: Pt/Ti mini-mesh. Anolyte: 1 M  $\text{CH}_3\text{OH}$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution. Catholyte: 0.5 M  $\text{H}_2\text{SO}_4$  solution. Temperature: 80 °C.

the cell rotation is claimed to enable rapid removal of water formed at the cathode by oxygen reduction and gives good mass transport of oxygen from the air to the cathode, thereby improving power performance and energy efficiency.

Rotating cells have also been proposed in the field of batteries. A metal air battery with rotating cylindrical electrodes has been patented [43], which uses a cylindrical air cathode and an outer cylindrical metal cathode separated by an aqueous sodium hydroxide electrolyte. This cell assembly is rotated around a central axis and produces a good mass transport environment for operation in the example quoted of an aluminium air battery. Rotation of the cell at up to 600 rpm gives a gravitational effect of 30G which is claimed to reduce the internal resistance by more than a factor of six.

A patent describes a rechargeable, electrochemical generation apparatus using the example of the Ni Zn battery [44]. The cell consists of an array of bipolar nickel-zinc electrode cells in a stacked, serially connected configuration for providing improved reliability and charge-discharge cycling capability. The improved reliability is targeted at the improvement in the zinc electrode cyclability wherein rotation improves the mass transport behaviour during charge and discharge, which minimises the build up of Zn metal dendrites, enabling improved

cycling numbers. The power source has a tightly packed cell stack, of thin, bipolar, flat annular electrodes which are provided with insulating seal rings at their inner and outer rims which can be rotated around a centre hollow shaft at high speed. The electrolyte is fed from a central shaft, into each cell formed by the electrodes and bound by the seal rings, through holes in the inner isolation ring of each cell and flows through the cell and out through holes in the outer isolation ring of each cell. The electrolyte may also be pumped with a cyclic pulsed mode of operation to further intensify mass transport.

### 3.2. Magnetic fields

The influence of an applied magnetic field on the operation of an electrochemical cell has been studied for over 40 years [45,46] and the field of magnetoelectrochemistry has been explored but not been widely developed. In general the field of MD has been pursued through the effect of magnetism to, in conjunction with an applied current, facilitate convection of fluid near electrode surfaces and to cause the motion of paramagnetic particles in solutions. These two effects come about by the generation of the so called Lorenz and Kelvin forces respectively. There has thus been significant interest in these and related effects, including possible practical applications. The effect of a magnetic field on electrolyte motion and on the gases produced during electrolysis was reported by Cousins et al. [47] by motion camera. The magnetic field reduced the volume of hydrogen gas collected during chromium plating. A magnetic field also produced significant effects on the compactness of chromium deposits.

#### 3.2.1. The Lorenz force

Dash and Takeo studied the effects of a uniform magnetic field applied to one electrode in a flow cell and found that the cell potential was either increased or decreased, depending on the relative orientations of the magnetic field, the electric field, and the flow. The change of the cell potential is directly proportional to the magnetic field strength and the flow velocity [48].

The enhancement effect of a magnetic field on an electrochemical reaction is associated with the magnetohydrodynamic (MHD) convection that is induced by the Lorenz force and the subject has been briefly reviewed by Monzon [49]. The magnetic field effect that induces convection in an electrochemical cell, by MHD is illustrated in Fig. 10. The magnetic field  $B$  acting in the cell externally, essentially unaltered by the flow of electrolyte or current, interacts with the local current density,  $i$ , induces a flow that tends to reduce the diffusion layer thickness and enhance mass transport. The limiting current increases due to the localised magnetic stirring of the electrolyte. The resulting Lorentz force is given by the product of the current density and the magnetic field,  $B$ :

$$F_L = i \times B \quad (16)$$



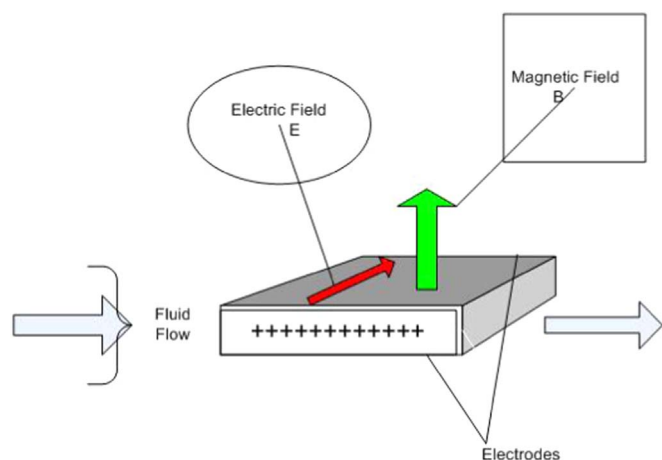


Fig. 10. Magnetic field and electrical potential effect on flow.

The force is zero when  $B$  and  $i$  are parallel, and it is the largest when they are orthogonal. During for example electrodeposition, the Lorentz force may be comparable in magnitude to the buoyancy force driving convection. With a magnetic flux of  $B = 1.0 \text{ T}$  ( $\text{NA/m}$ ) the force acting on a fluid volume at say a current density of the order of  $100 \text{ mA/cm}^2$  is  $1000 \text{ N m}^{-3}$ . The flow pattern can therefore be modified by applying a magnetic field and, although these forces are not large and may not create large-scale convection in comparison to that achieved by mechanical agitation, they can create localised convection effects where there is a localised area of relatively high current density [49]. Where there is a localised region of high current density, say at the edge of an electrode or around an area of raised surface or around a bubble the relation between Lorentz force and local current density flow patterns can be induced magnetically on a small scale that may not be otherwise attainable (Fig. 11). Also MHD can result in electrolyte flow in microfluidic channels, where transverse redox currents are flowing [50,51].

Magnetic fields have been shown to influence a number of electrochemical processes and several studies have investigated MHD in the

area of metal electrodeposition [50–52]. During metal electrodeposition an uneven growth at the cathode results in a locally non-uniform current distribution, creating secondary micro-MHD vortices around growing asperities that protrude into the diffusion layer, as illustrated in Fig. 11c [53,54]. Micro-MHD can result in the improvement of hard nickel electrodeposits containing alumina nanoparticles when they are pulse-plated in a magnetic field, which is said to be partly due to the effective removal of hydrogen bubbles during plating [56].

In addition to enhancing the electro-deposition rate via the MHD effect, it also can influence the morphology, texture, roughness and dendritic character of electrodeposits [57] which depend upon the orientation of the field relative to the cathode surface.

Magnetic fields applied parallel to the electrode tend to suppress three-dimensional nucleation and dendritic growth, but they promote faster, two-dimensional growth and smoother deposits as reported by Aogaki and Morimoto [55]. A perpendicular field usually produces rougher deposits. The magnetic field can also induce preferred crystallographic texturing in metallic electrodeposits [58,59]. In general the surface roughness of electrodeposited films may be enhanced [60] or reduced [59] but the film thickness is almost always enhanced as a result of improved ion transport [59,61].

A magnetic field has been found to modify the morphology of individual crystals via micro-MHD convection are [62,63] and the morphology of electrodeposited materials [64,65]. In addition to having an influence on growth, a magnetic field will influence nucleation of gas from solution and metals, where the number of nucleation sites often increases in the presence of the field, irrespective of its orientation [63,66]. Micro-MHD has been demonstrated for the improvement of hard nickel electrodeposits containing alumina nanoparticles; alumina content of the hard coating is increased, and its hardness increased when they are pulse-plated in a magnetic field, which is said to be partly due to the effective removal of hydrogen bubbles during plating [67].

The magnetic fields can also have an effect on anodic processes, where it can result in a shift in rest potential [68] and enhanced corrosion [69,70] of magnetic and nonmagnetic electrodes. With ferromagnetic electrodes such as Fe, localised retention of Fe ions and a local increase in pH, can result in a decreased corrosion current

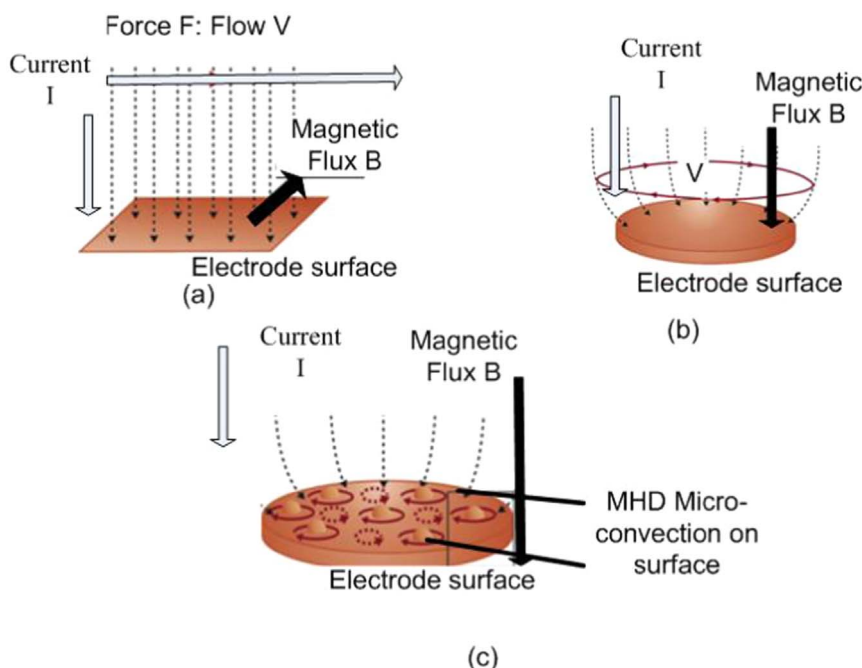


Fig. 11. Flow patterns induced by MHD (after Monzon and Coey [49]). a) Field parallel to the electrode surface. The main flow is parallel to the surface; b) Field applied, perpendicular to the electrode surface- the primary MHD flow is a vortex around the rim, c) Secondary micro-MHD vortices created around protruberances on the surface when the field is perpendicular to the electrode surface.

and a cathodic shift of the rest potential [71,72].

Magnetic fields have been shown to affect charge transfer reactions taking place on confined redox probes [73] and to influence anodic polymerisation [74] with modifications in polymer texture, open or crystalline, achieved by varying the direction of the field [75].

Mogi et al. have recently demonstrated that magnetically prepared Ag or Cu electrodes exhibit a high sensitivity towards certain enantiomeric amino acids, offering a novel route for the synthesis of biomolecules with a high enantioselectivity [76]. The use of MHD include the control of corrosion and electropolishing in which it can improve the surface finish of electro-polished biocompatible metallic alloys [77]. Interestingly it is reported that nickel metal hydride batteries performance can be enhanced by > 25% when compared with the performance without magnetic fields [78].

### 3.2.2. The Kelvin force

As described above, most of the early work in magneto-electrochemistry was devoted to a study of the effect of the Lorentz force on convection on the scale of the electrochemical cell [49]. MHD can also induce forces acting directly on paramagnetic species in the electrolyte, i.e. the Kelvin force. The Kelvin forces associated with magnetic field gradients are always present because any redox process where a single electron is transferred generally involves paramagnetic species [79]. The magnetic species in an electrolyte are usually paramagnetic cations, free radicals or molecular species with unpaired spin such as O<sub>2</sub>. An applied field H induces a magnetization  $M = \chi H$ , where,  $\chi$  is the dimensionless Curie-law magnetic susceptibility of these species in aqueous solution [79]. When the magnetic field is non-uniform, there is a force on the dissolved magnetic species which tends to draw it into regions where the magnitude of the field is greatest. The Kelvin force density (also known as the magnetic field-gradient force or magneto-phoretic force) is proportional to the paramagnetic susceptibility of the species in solution.

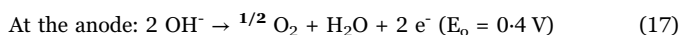
Unlike the Lorentz force, which drives magnetohydrodynamic (MHD) convection via the electric current (which the force itself may be modest), the Kelvin force can be significant in the presence of a non-uniform distribution and hence can be expected to create convection in the vicinity of an electrode where there is a paramagnetic concentration gradient [79]. The magnitude of the magnetic force can be of the order of  $\sim 1000 \text{ N m}^{-3}$ , which is sufficient to affect convection [79]. The field gradient and concentration gradient must be non-collinear for vorticity to appear. Thus when the field gradient is parallel acting along the surface of an electrode, the resulting convection will thin the diffusion layer and the current is enhanced due to the MHD induced force [79].

Magnetic field gradients near the surface of the working electrode have been exploited to pattern electrodeposits using magnetised metal [80–83]. Platinum thin films have been deposited on porous alumina membranes filled with an array of electrodeposited magnetic nanowires to create an ORR [84], which is of interest for fuel cells. These so-called, field gradient electrodes enhance the current density for the ORR in oxygen-saturated solutions [85]. Micron-size ferromagnetic materials have also been embedded in the electrode [86,87] or used as surface modification of the electrode [88] to improve the efficiency of fuel cells by magnetising these nanostructure electrodes.

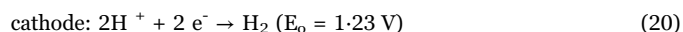
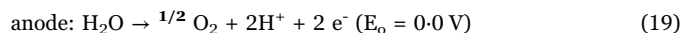
### 3.2.3. Gas evolving electrochemical reactions

There is an abundance of electrochemical cells in which at one or both of the electrodes a gas evolution reaction occurs, frequently as the main product but also as a by-product as a result of Faradaic efficiencies less than 100%. Probably, the most well known examples are electrolysis of water, which produce hydrogen at a cathode and oxygen at an anode:

In an alkaline electrolyte:



In acid electrolytes based cells, typically using a solid polymer electrolyte (and not an aqueous electrolyte, such as sulphuric acid), the electrode reactions are



A large amount of research has been conducted in order to understand the phenomena involved in the water electrolysis processes to assist in improving the performance of the technology. From this an improved understanding of the convective effects, the mass transfer processes and the energy losses due the bubble layers generated at a gas evolving electrodes has been achieved [89,90]. It has been shown that increased forced convection in the electrolyte has a significant influence on reducing the fractional bubble coverage. The surface area fraction covered by bubbles is a very important parameter which can control the highest (limiting) current density. In an electrochemical gas evolving reaction the reaction on the active sites of the electrode surface leads to supersaturation of the gas molecules which then leads to the formation of gas bubbles. These bubbles then grow gradually with time until a critical size is achieved, at which the bubbles are released from the electrode surface [91]. In practical electrolytic cells, bubbles attached to an electrode surface cover active sites during nucleation and growth. The presence of bubbles will disturb current distribution, as sites become gradually filled and then emptied during bubble lift-off, as well as isolating active sites from the reaction ions. These phenomena lead to large reaction overpotentials and also to high Ohmic voltages. The overpotential associated with bubble coverage has been described by using a modified Tafel overpotential relationship wherein the actual current density is defined using a bubble coverage  $\theta$  [91]:

$$\eta = a + b \log(i_0) \quad (21)$$

Where  $i_0 = I/A(1 - \theta)$

Where  $\theta$  is bubble coverage ratio on electrode surface.

This can be written in terms of the overpotential unaffected by surface coverage,  $\eta$ , and the surface coverage as [91]:

$$\eta_0 = \eta - b^* \log(1 - \theta) \quad (22)$$

There have been a number of studies of gas bubble formation on electrode surfaces. Krenz [92] observed that coverage increased with current density as might be expected and also that an increase in temperature also increased bubble coverage, presumably as a consequence of lower gas solubility. Bubble coverage was observed to increase from 0.06 to 0.2 (at 25 °C) over the current density range of 100 to  $10^4 \text{ A/m}^2$ . Balzer and Vogt also [93] also reported bubble coverages of around 0.2 at  $1400 \text{ A m}^{-2}$  to 0.22 at  $2000 \text{ A m}^{-2}$ .

In addition during bubble growth and release, the bubbles induce micro-convection which acts to displace electrolyte in a radial direction. Thus more rapid bubble release can impact on creating a more efficient electrolysis process; gas release increases availability of active sites and enhances mass transport. The analysis of bubble induced polarisation is largely empirical as it relies heavily on the ability to predict the bubble coverage, as well as the mass transport behaviour at the electrode. Thus correlation of the type of Eq. (22) are used to interpret experimental data. Aldas however attempted to theoretically describe the behaviour and showed [94] that the adsorbed bubble layer on an electrode surface, greatly decreased the gas evolution rate.

The effect of bubble formation on Ohmic voltage losses is linked to two general effects. Bubbles increase in size with time and when they reach a certain size they detach from electrode surface into electrolyte and a second bubble layer can be formed in the vicinity of electrode surface. The behaviour or movement of bubbles and the electrolyte in this region depends upon the orientation of the electrode and velocity

of the electrolyte fluid. In vertically orientated electrodes the relative motion between gas phase and liquid phase is such that bubbles ascend in the upward direction due to buoyancy and density difference between gas and liquid. Meanwhile, bubbles accumulate in this direction and can result in a bubble curtain of increasing size (Fig. 4). The extent of bubble curtain formation depends upon the fluid flow behaviour and whether or not turbulence is induced, which would tend to disrupt the formation of the bubble curtain and propel bubbles into the bulk electrolyte, tending to form a more uniform distribution of bubbles in the direction of the average current flow between the electrodes. Meanwhile, an increase in the Ohmic voltage drop from insulating bubble layers on an electrode surface or bubble swarms is achieved. Generally, the conductivity of electrolyte with dispersion of bubbles in electrolyte are represented by the Bruggeman equation [95]

$$\kappa = \kappa_0 (1 - \epsilon)^{1.5} \quad (23)$$

Where  $\epsilon$  is the void fraction of bubbles.

This void fraction is very system specific and is a function of solution composition, pressure, current density, bubble size, bubble layer thickness, electrode separation and fluid flow. Clearly, bubbles dispersed in electrolyte in the vicinity of electrode can cause large electrolyte resistance and high Ohmic voltage drop as there will be a large void fraction of bubbles in this region. The negative effect of bubble dispersion becomes more serious with an increase in electrode height and with a slower motion of electrolyte. A lower void fraction increases the effective conductivity of electrolyte and decreases the Ohmic voltage loss. Thus any means that reduces the bubble layer thickness can potentially benefit electrolyser performance.

In general the application of a magnetic field during water electrolysis process is seen as a means of enhancing fluid convection and bubble disengagement and overall, benefiting mass transport at the electrode surface.

This general behaviour has been identified as having potential for process intensification of gas evolution from electrode surfaces. Significant amounts of research have focused on water electrolysis due to its importance in electrochemical technology in general but also for the future development of a hydrogen economy. This in itself has been the subject of a review [96].

Gas evolution reactions occur in the three-phase (gas–liquid–solid) interface formed at the electrode when a potential is applied with a magnitude greater than the equilibrium potential that instigates the flow of current. The nucleation, growth and detachment of bubbles are affected by surface tensions of gas–liquid, gas–solid and liquid–solid. When a magnetic field is applied perpendicular to the electrode, a drag force is induced to increase the contact angle which promotes bubble detachment from the electrode surface [97]. Therefore, the detachment velocity of bubbles is accelerated due to MHD convection, especially when relatively large magnetic field intensities, ( $> 1.0$  T) are applied as has been observed for oxygen evolution on transparent electrodes. The increased detachment velocity reduces bubble residential times on the electrode surface and consequently reduces bubble coverage; ultimately benefitting the electrode reaction rate. [98,99].

Iida et al. [100] demonstrated that by superimposing a high magnetic field of 5.0 Tesla during water electrolysis in alkaline (KOH) and acidic ( $\text{H}_2\text{SO}_4$ ) electrolytes, a large reduction in cell voltage can be achieved. The effect was especially beneficial in an alkaline solution and at high current densities of 2–4 A/cm<sup>2</sup>, with voltage reductions of some 500 mV achieved at 1 A/cm<sup>2</sup>. The decrease in the IR voltage depended on the concentration of electrolyte solutions. In a magnetic field, the oxygen overpotential fell more than the hydrogen overpotential and overall, the benefits of the magnetic field were seen with flux intensities of 1–2 T, with higher values not creating much more of an improvement.

Matsushima et al. [101] studied mass transport rates and hydrogen supersaturation (S) at the interface of electrode-electrolyte. With the

application of a magnetic field mass transfer coefficients increased and the associated hydrogen supersaturation (S) fell with an increase in intensity of the magnetic field intensity, especially at higher current density (Fig. 6). The greatest benefit of the magnetic field is seen with the application of 1.0 T, where typically an order of magnitude increase in mass transfer coefficient was achieved, e.g. from around  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  m/s at a current density of 1 A/cm<sup>2</sup> under their experimental conditions. The supersaturation fell dramatically under these conditions from around 145 to 20. These changes are accredited to the magnetic field promoting mass transfer of dissolved hydrogen to release supersaturation from the electrolyte in the vicinity of the electrode.

Matsushima et al. [102] who found that the average bubble layer thicknesses (d) were reduced by magnetic field during water electrolysis. With an applied field of 1.0 T an approximate 30–50% reduction in average layer thickness can be achieved; with further, but not as significant, decrease in thickness with higher magnetic fields up to 5 T. Hence the magnetic field promotes the rapid disengagement of bubbles from electrolyte and calculated void fractions were also shown to decrease from 0.40 to 0.28 for hydrogen bubbles and from 0.48 to 0.41 for oxygen bubbles [102].

The effect of a magnetic field on the hydrogen evolution reaction (HER) during water electrolysis in 0.1 M  $\text{Na}_2\text{SO}_4$  solution has been reported [99]. The desorption of hydrogen was enhanced in terms of achieving an increased current density since more active sites become available with the magnetic field, irrespective of the magnetic field orientation with respect to the electrode surface. A reduction of the mean bubble size and occurrence of a narrower bubble size distribution and reduction in fractional bubble coverage, which were accredited to the Lorentz force driven convection induced by a magnetic field.

### 3.2.4. Hydrogen generation

Magnetic fields have been applied for decades to promote the production of water by electrolysis. Harris describes a cell that combines a permanent magnet and an electro-magnet to produce hydrogen from sulphuric acid in a patent [103].

The magnetic nature of different electrode materials has been investigated [104] by comparing the performance of nickel (ferromagnetic), platinum (paramagnetic) and graphite (diamagnetic) electrodes during water electrolysis under the influence of a magnetic field. A ferromagnetic electrode, such as nickel, was better cathode materials than the paramagnetic platinum and diamagnetic (graphite) under a magnetic field for electrolysis with KOH electrolyte at room temperature. With an electrode spacing of 2 mm and a voltage of 4.0 V, nickel electrodes (ferromagnetic) increased the current density by 14.6%, and platinum electrodes increased the current density by 10%. There was no beneficial effect with graphite although current densities were low with this material. In principle if electrolysis is carried out with a ferromagnetic material the influence of a magnetic field has a greater benefit than using more expensive Pt electrodes. Thus if the ferromagnetic material is stable this can present a lower cost option. It was also shown that the effect was more beneficial with narrower inter-electrode gaps. In addition it was also shown that it is important to have the Lorentz force induced in an upward direction and not a downward direction which presumably hinders bubble rise from the electrode.

Lin investigated the effect of a magnetic field and pulsed potential on hydrogen evolution using nickel electrodes [105]. They showed that the Lorentz force of the magnetic field changes the direction of convective flow of the electrolyte and, that generally a pulsed potential and magnetic field simultaneously enhance hydrogen evolution performance.

### 3.2.5. Microfluidics

The ability to perform laboratory operations on small scales using miniaturized (lab-on-a-chip) devices has applications in areas such as chemical synthesis, the study of complex cellular processes and medical diagnostics. Designing and fabricating such systems is extremely

challenging, and in such devices provision of suitable microfluidics is important in miniaturization as it enables the control of movement of tiny fluid volumes [106,107]. Microfluidic stirring or mixing has been demonstrated using methods such as electro-thermal, induced charge electro-osmosis, and liquid on liquid techniques [108]. Many approaches either require a complex device design involving flow channels or need a high voltage, operation [109]. The applications of MHD forces to pump, stir, and control fluids have been used historically mainly with highly conducting fluids like liquid metals and ionised gases [110]. Micropumps have been created [111–115] using MHD with silicon and ceramic substrates to move liquids around small conduits. A MHD continuous flow micro-reactor with three thermal zones to facilitate thermo-cycling has been applied to DNA amplification [116]. A circular open tubular chromatographic system has been designed based on the circular flow motion induced by MHD [117,118]. A toroidal MHD stirrer in which the direction of the flow reversed periodically has been reported [110].

MHD requires the application of a relatively high voltage, which can create problems associated with electrode corrosion and bubble generation [119,120]. By introducing suitable oxidisable or reducible chemical species, a so-called redox-MHD circumvents these problems in which the redox species enable generation of a Faradaic current at lower overpotentials, thus avoiding the problems commonly encountered with traditional MHD pumps in supporting electrolyte alone [121–123]. MHD driven flow through ceramic channels with built-in gold electrodes has been demonstrated using different solution compositions, potential differences, and intensity of the magnetic field [124]. A current density of around 3 mA/cm<sup>2</sup> generated fluid velocities 0.1–0.3 mm/s in 0.3 cm × 0.6 cm channels, at a cell potential difference of only 0.3 V.

A relatively easy-to-use fluid pumping technique of redox MHD has been demonstrated by Zahore, that induces localised fluid circulation [125]. Microfluidic rotational flow was obtained under laminar conditions (Reynolds number < 1) between concentric disc-ring microelectrodes, when a constant potential was applied across the electrodes in the presence of an external magnetic field.

### 3.2.6. Ultrasonics

Sound comprises longitudinal waves that cause compression and rarefaction cycles as they pass through a medium [126]. Audible sound covers the frequency range from approximately 16 Hz to 16 kHz and ultrasound frequencies are higher and generally called ‘power’ ultrasound (20 – 100 kHz). Power ultrasound is used in ultrasonic cleaning baths and plastic welding. Frequencies around and above 1 MHz are used for diagnostics, medical scans and other analytical applications.

In liquid media, ultrasound can cause ‘acoustic streaming’ and/or the formation of cavitation bubbles, depending upon several parameters; ultrasonic power, frequency, sonic source characteristics, and liquid characteristics such as viscosity, volatility, presence of dissolved gases or other nucleation sites [126]. The formation and decay of cavitation bubbles have been reported to involve transient extremes of temperature and pressure, and the bubbles can form micro-jets that impinge towards a surface..

A number of possible effects of ultrasound on electrochemical systems or heterogenous electrode surfaces have been identified [126]:

1. An improvement of hydrodynamics and *species* mass transport
2. Modification of concentration gradients at various points in the reaction profile, and consequent switching of kinetic regimes which effect mechanisms and reaction products
3. A cleaning and abrading effect upon an electrode surface
4. Altering the nature of surface, electrode coatings
5. Sonochemically-induced reactions of electrochemically generated intermediate species
6. The formation of electrochemically reactive species not formed in the absence of ultrasound.

The influence of ultrasound on electrochemical processes will depend upon both ultrasonic parameters and a range of electrochemical parameters; e.g. solvent, electrolyte, electrode material, cell and electrode geometries, electrode potential and any dynamic modulation of potential or current density. Also the presence of quenching or trapping agents, may be varied to affect the course of electrochemical reaction of the substrate molecule [127].

The application of ultrasound to electrochemical processes dates back to the reported effect on concentration polarisation by Moruguchi, in 1934 [128]. More recently sonoelectrochemistry has become of interest due to the impact of the variety of effects it induces on electrochemical processes, linked to the generation, growth and collapse of microbubbles in the electrolyte and, close to an electrode surface, the formation of high velocity microjets of liquid toward the surface [129–132]. These phenomena can decrease the electrode diffusion layer thickness [133] and can improve the overall mass transport, increasing reaction rates [134], as well as inducing chemical effects [135] associated with the generation of radical from the sonolysis of the solvent.

The applications of ultrasound in electrochemical systems are described in detail by Pollet [136] and include: metallic coating organic electrochemistry, environmental remediation, corrosion, electropolymerisation, nano-materials fabrication, inorganic electrochemistry such as hydrogen evolution and electrocatalyst fabrication.

Li et al. [137] showed that the effect of ultrasonic field on water electrolysis in alkaline solution decreased the cell voltage, especially at higher current density and with lower electrolyte concentration. The efficiency of hydrogen production was increased by 5–18% and energy reduction by up to 10–25%, at higher current density under an ultrasonic field. Zadeh [138] reported similar effects of ultrasound on hydrogen evolution in alkaline electrolytes. In general the effect of an ultrasonic field on gas evolution reactions can affect the disengagement of gas bubbles from electrode surface due to the intense agitation effect of cavitation bubbles. Therefore, fine bubbles are formed more easily under an ultrasonic field, with the periodic collapse of the cavitation bubbles, which can reduce bubble formation overpotential and Ohmic voltage. The effect of an ultrasonic field on hydrogen production with a polyvinylidene fluoride-grafted 2-methacrylic acid 3-(bis-carboxymethylamino)2-hydroxyl-propylester bipolar membrane (PVDF-g-G-1 BM) was shown to be improved in comparison to that without ultrasound [139].

A recent patent has described an apparatus and method to dissociate water into hydrogen and oxygen gases by electrolysis from the individual and balanced cumulative application of acoustic cavitation, a high-energy magnetic field and specific wavelength infrared energy [140]. The device is claimed to provide improved energy efficiency in water electrolysis due to the combined field effects.

## 4. Power from fluid flow

Studies on the effect of magnetic fields on electrochemical processes have in general focused on the convection effects created in the electrolyte by the Lorentz force and how they help improve mass transport and reduce concentration polarisation during plating and other reactions. As described above in the area of microfluidics, the use of a magnetic field in conjunction with an electrochemical field can induce fluid motion. Conversely the application of a magnetic field should enable the production of an electrical field and/or current flow. Wright and Van Der Beken [141] have experimentally observed that the Lorentz force acting on the sodium and chlorine ions in salt water, flowing in a circular pipe, gives rise to a Faradaic voltage. This voltage can be expressed as the product of *B* and *D*, where *D* is the diameter of the circular pipe. Furthermore, Geselowitz [142] has shown that this result is valid for any velocity profile, provided the flow is axially symmetric. DeLuca showed, from a theoretical analysis, that the magnetic effect could generate current through the flow of dilute



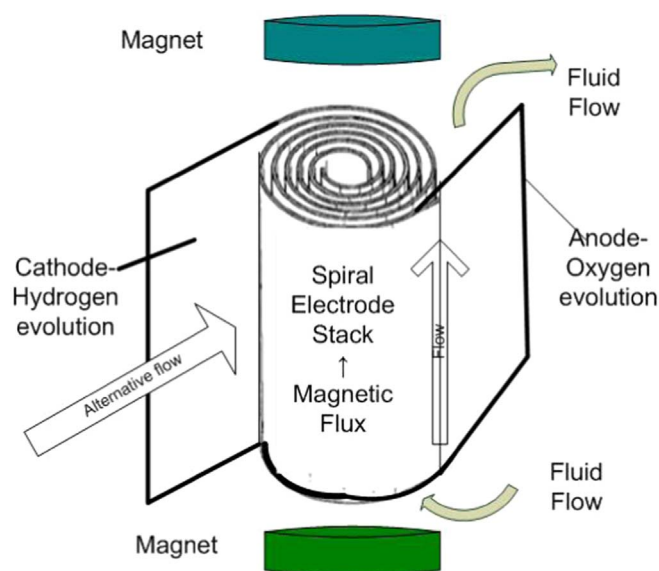


Fig. 12. Spiral electrode cell for water electrolysis.

sodium chloride in a narrow channel bounded by two electrodes [143]. This model generally validated Van Der Beken measurements and showed that power of the order of 10 of mW's could be generated; which is theoretically capable of electrolysing water.

The effect of a magnetic field on a spiral configuration of electrolyzers (Fig. 12) has been reported in a patent by Hasebe [144]. In this study, the two electrodes are arranged co-axially and a magnetic field was applied using ring magnets at either ends of the axis of the electrodes. Sodium hydroxide electrolyte flowed, (using a high speed pump) along the axis of the cell. The data in the patent claim to create over 20 more hydrogen and oxygen gases than predicted by Faradays Law of electrolysis. The reported data claimed that with a current of 30 amps (voltage 2.8 V, 298 K) a hydrogen production rate of 78 cc/s cf Faradays law prediction of 3.8 cm<sup>3</sup>/s (at 298 K). Unfortunately the work does not appear to have been followed up with more studies.

Spiral configurations of electrolyzers have been previously used in applications such as metal recovery in for example the Swiss roll cell [145] and generally may be considered to present an opportunity to capitalise on process intensification with magnetic fields. For hydrogen electrolyzers it would be advantageous to introduce membrane separators to enable separate hydrogen and oxygen generation rather than the mixed gases of hydrogen and oxygen (so called brown hydrogen) [4].

#### 4.1. Power from rotation

Conventional electrolyzers use electricity from the grid and in principle they can use a source of renewable energy (e.g. via wind) and a number of demonstrations of this approach are underway [146]. In powering the electrolyser there is a need for AC to DC conversion and potentially transforming the voltage from a high to a low potential (low current to high current). This conversion and transmission results in efficiency losses and ideally should be kept to a minimum. Bockris and Guttman suggested [147] that electrolysis could be carried out by providing the potential (and power) by magnetic induction within the electrolyser, i.e. in a similar way to the classic homo-polar generator demonstrated by Faraday [148].

There are potentially several ways in which the electrical potential could be generated and one method is to use a disc in which sufficient potential difference is generated between two regions on the disc to drive the electrolysis (Fig. 13). Using this concept, Ghoroghchian and Bockris [149] developed a homopolar stainless steel disc electrolyser (30 cm), which was rotated at a speed of 2000 rpm under a 0.86 T magnetic field in a 30% KOH solution. In general the rotation of the

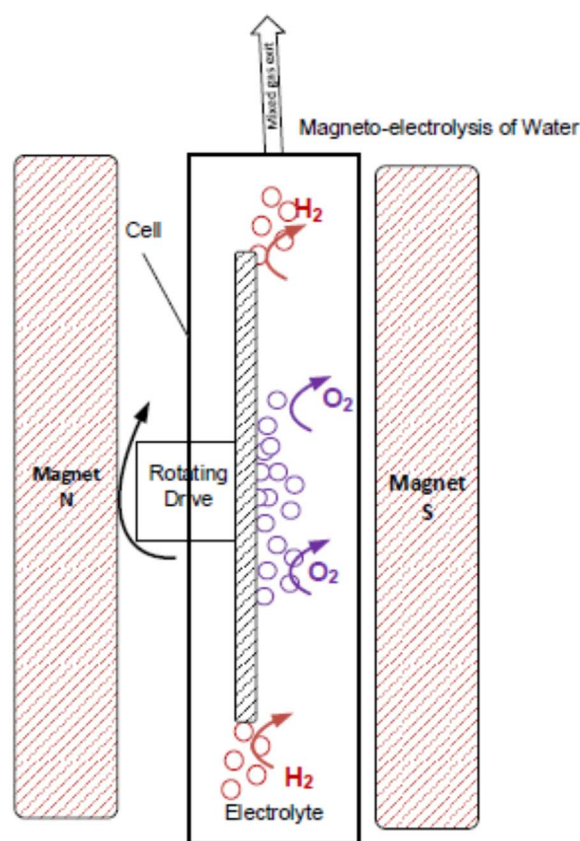


Fig. 13. Homopolar Generator for Water Magneto-electrolysis.

disc in an electrolyte has to overcome the viscous forces (shear) as well as magnetic torque. To overcome these energy losses in rotating the disc it is possible to rotate both the disc and the fluid in a cassette or rotate the complete cell, which effectively reduces the relative motion of the disc and electrolyte to zero.

Bockris estimated [147], from basic principles, that the magnetic field required to create the energy required to produce a unit cubic metre of hydrogen at a similar energy consumption to an electrolyser (i.e. at 2.0 V) was of the order of 11 T. This calculation ignored any IR voltage losses that may occur in the electrolyte. A magnetic field of 11 T is in the domain of supermagnets which are expensive. As an alternative to high Teslar magnets, Bockris suggested that a separate homopolar generator be used to provide the cell power either continuously or as a pulsed voltage source. It is stated by Bockris that the use of pulsed power is a more efficient way of producing hydrogen by electrolysis.

Iwakura, et al., demonstrated magnetoelectrolysis using a rotating cell and a permanent magnet, using a cell consisting of the shaft, drum (made from Cu coated stainless steel) and two caps rotated in an externally applied magnetic field [150,151]. A DC potential difference was generated between the shaft and drum, as a result of the Lorentz forces acting on the charged particles, which were directly proportional to the rate of rotation and the magnetic flux density but independent of the kind of electrolytes. A current density, of the order of 1 mA/cm<sup>2</sup> flowed through the system when the shaft and drum were externally connected to each other via a resistance. The current vs. potential difference curves obtained were the same as those obtained by applying an electric field externally.

A Russian patent in 2007 [152], describes a water electrolyser using a rotating cell consisting of a shaft surrounded by an annular ring. The outer electrode ring and inner electrode on the shaft are electrically connected. Electrolyte is fed via a central inlet pipe inside the rotating shaft. A magnetic field is applied perpendicular to the direction of rotation (Fig. 14). No performance data are given in the patent.

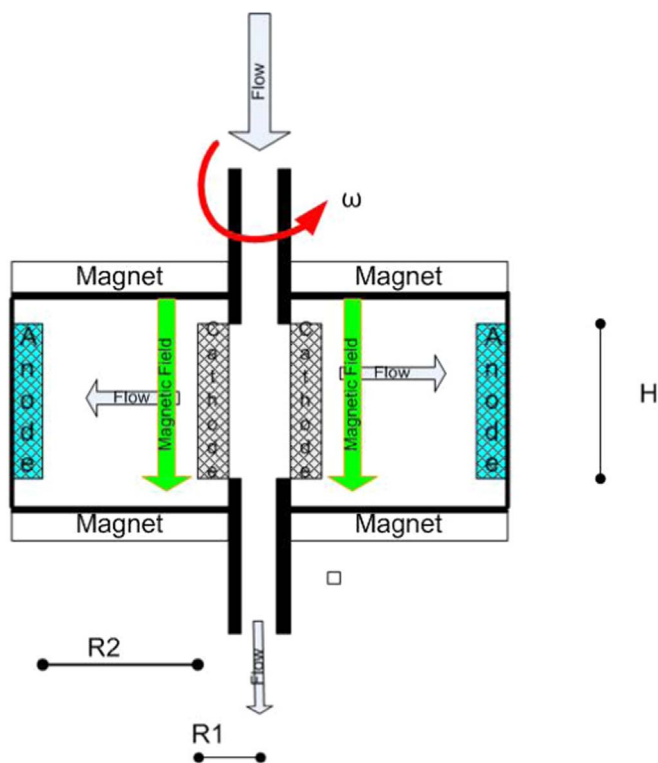


Fig. 14. Rotating concentric electrode electrolyser with magnetic field.

#### 4.2. Theoretical analyses

Rotating electrochemical cells, utilising the action of centrifugal forces, have been investigated for a number of processes and including, determination of transport numbers of ions [153], and to improve the performance of important electrolytic processes such as water electrolysis and the production of chlorine [34,35], etching of semiconductor materials [154], in electrochemical power sources [155] and to control the rate of electrochemical polymerisation. In general the field has been given the term “chemistry in the centrifugal fields” [156].

The application of a centrifugal field has been demonstrated to intensify the water electrolysis process. Data collected from the linear sweep voltammetry and steady-state measurements showed that an anode potential reduction of up to 0.18 V, a cathode potential reduction of up to 0.20 V, an Ohmic voltage reduction of up to 0.25 V and a cell voltage reduction of up to 0.45 V at 300 mA/cm<sup>2</sup>, were achieved at a relative acceleration rate of 190G and 80 °C, compared to those in stationary conditions. The saving in cell voltage, and thus energy consumption, are significantly larger than the relatively small amount of energy required to rotate the cell. The above observations were modelled (Fig. 15) using an empirical approach [37]. The model correlated the cell performance to relative acceleration rate and considered the effects of the KOH concentration and the cell temperature. The experimental measured electrode potentials and Ohmic voltage losses data were explained satisfactorily by the empirical correlations. These correlations were based on a rotary cell consisting of two parallel rectangular channels, with electrodes facing a membrane, which separates anolyte and catholyte. In the centrifugal field, the mixture of gas and electrolyte rotates at the same speed as the cell body and a rapid bulk radial flow of the gas bubbles is inwards to the axis. The mathematical model was developed to examine the influence of centrifugal fields on the electrochemical behaviour of the rotary cell with gas evolving electrodes. The model included the effect of centrifugal fields on electrode polarisation, cell voltage, solution voltage drop and mass transfer coefficient, are described in the following sections. The approach used developed an expression for the cell

voltage of the rotary cell considering mass transfer and bubble effects, respectively, and then incorporate them into a centrifugal cell model [157]:

$$E_{\text{Cell}} = E_{A,e} + E_{C,e} + a_A + a_C + (b_A + b_C) \log [1.0384n F D r^{1/3} (L/2 + r)^{1/3} \omega^{2/3} / (L^{1/3} v^{2/3})] + \eta_A + \frac{1}{2} \eta_C^{1/2} + [1.0384 n F D r^{1/3} (L/2 + r)^{1/3} \omega^{2/3} / (L^{1/3} v^{2/3})] (L/\sigma_A + L/\sigma_C + \delta_M/\sigma_M) + S [1.0384 n F D r^{1/3} (L/2 + r)^{1/3} \omega^{2/3} / (L^{1/3} v^{2/3})] / \sigma [1 - 1.5576 R T D r^{1/3} (L/2 + r)^{1/3} \omega^{2/3} / (L^{1/3} v^{2/3}) (P - P^\circ)] \quad (23')$$

It is known that electrochemical systems with the electrodes, located in the centrifugal field at different distances from the rotation axis, give rise to an emf; the value of which depends on several factors but notably, the rotation rate of electrochemical cell and on the distances between the rotation axis and the electrodes [157].

The first studies of the effect of gravitational field on the emf of galvanic cell, showed that small emfs could be generated. Placing the electrochemical cell into a centrifuge could significantly increase this potential to several mV's which was experimentally supported by Des Coudres [158] and Tolman's [159], in which it was shown that the emf increased proportionally to the square of angular rotational rate in later studies [159].

Bogradev [157] has analysed the emf, which is generated in the rotating electrochemical cell and showed that application of magnetic field can increase the emf from several mV to several volts in a metal deposition/dissolution system. Their analysis gave rise to the following theoretical potential that arises from cell rotation:

$$E = \frac{\omega^2 [R_2^2 - R_1^2]}{2F} (M_+ t_+ - t_- (M_- - V_o \rho) - V_M \rho) \quad (24)$$

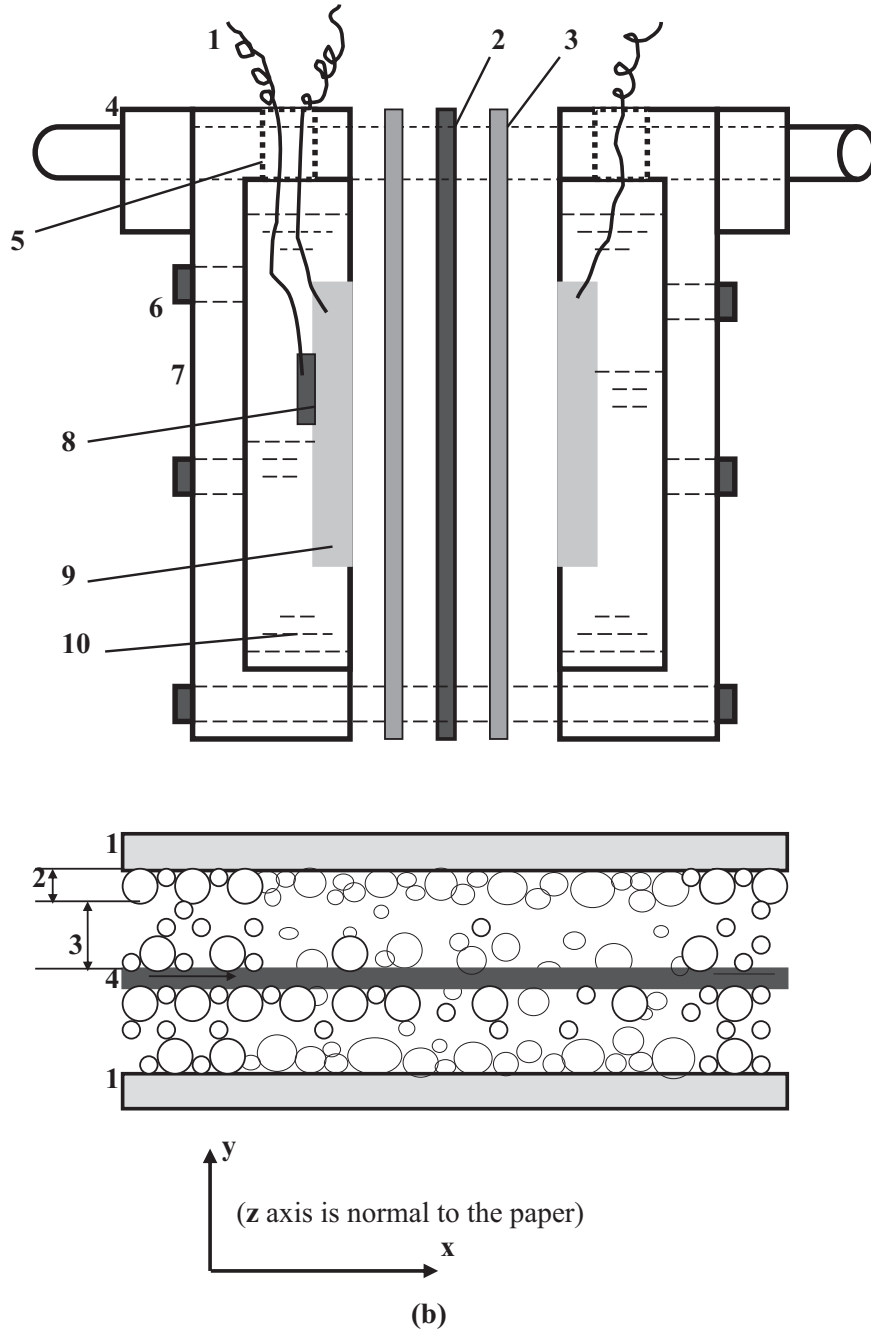
Where  $t_+ = D_+ / (D_- + D_+)$  and  $t_- = D_- / (D_- + D_+)$  are transport numbers of cations and anions respectively, and  $V_o$  and  $V_M$  are overall molar volumes of dissolved substances.

In addition they also showed theoretically that the potential generated by a magnetic field was given by

$$E_R = \int dr B \omega = \frac{B \omega [R_2^2 - R_1^2]}{2} \quad (25)$$

The obtained equation coincides with the equation for the potential difference between the central and periphery parts of disc rotating in the magnetic field that was reported in the literature [149,158]. The magnetic field causes movement of electron in the rotating metal disc, in contrast to the electrolyte solutions, in which ions are the mobile charge carriers. Comparing Eqs. (24) and (25), the effect of rotation rate on the emf is lower in the case of the application of a magnetic field compared with the separate use of physical rotation. However with the magnetic field, the emf is directly proportional to the magnetic induction, which provides for a significant increase in the emf generated in the rotating electrochemical cell. Note that in fact the emf generated would be the sum of the two emfs, given by Eqs. (24) and (25); although typically the magnetic field effect is more significant (Fig. 16).

Bogradev showed that the results calculated by Eq. (25) agreed well with the experimental data reported in [157]. For example, they showed that in sulphuric acid solution with rotational rate of 8000 rpm, and an average magnetic-flux density of 0.1492 T, ( $R_1 = 4$  mm, and  $R_2 = 22$  mm, the open circuit potential difference between two cylindrical electrodes in a rotating electrochemical cell was 29 mV which compares well with experimental values of 25–27 mV measured by Iwakura [151]. From the above equations it is possible to estimate the effect of cell rotation and magnetic field on potential difference between two electrodes in a rotating cell, where as shown in Fig. 17, it is possible to generate potentials of several volts which would be sufficient for electrochemical reaction without an applied external DC voltage.



**Fig. 15.** Model system for centrifugal cell. 1: Inlet and outlet; 2: Counter electrode current feeder (the counter electrode is directly contact the feeder); 3: Membrane; 4: Gasket; 5: Working electrode current feeder; 6: Working electrode; 7: Reference electrode; 8: Rotating axis; 9: Polypropylene block; 10: Belt hole; 11: Rotating direction.

Bogachev, later considered conditions that optimise the generation of power as function of rotation and applied magnetic field [160]. In this analysis they considered the relationships between the rotational rate of the electrochemical cell, its Ohmic resistance, a ratio between the inner and outer cylindrical electrode radii, a sum of cathodic and anodic potentials, and the mechanical energy, which is consumed for passing a prescribed current and overcoming friction forces, for operation of a rotating electrochemical cell. The analysis assumed that a certain electrochemical process with a prescribed efficiency requires an overall current, which requires a voltage  $E$  to be generated between the electrodes to overcome the sum of the anode and cathode overpotentials,  $\eta_T$ , and internal resistance,  $R$ :

$$E = \eta_T + I R \quad (26)$$

Where  $E$  is given by Eq. (25).

The internal resistance is defined by:

$$R = \ln[R_2/R_1]/(2\pi\kappa_E H) \quad (27)$$

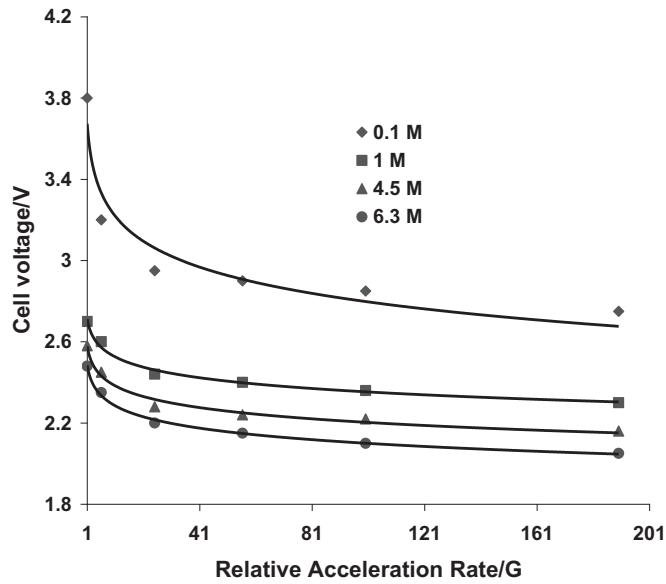
Where  $\kappa_E$  is the electrolyte conductivity and  $H$  the cell height.

The relationship for the current is given by [160]:

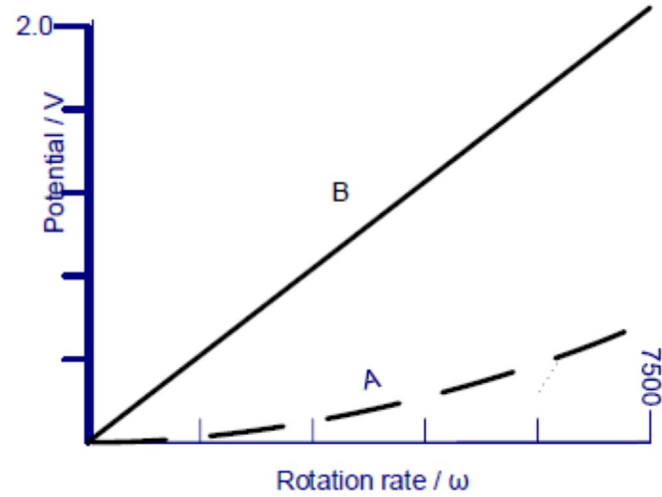
$$\frac{B\omega[R_2^2 - R_1^2]}{2} = I \frac{\ln(R_2/R_1)}{2\pi\kappa_E H} + \eta_T \quad (28)$$

From this equation it is possible to estimate the rotation rate required to achieve specific currents as a function of cell parameters. The analysis of Bogachev also enabled estimation of the total power required for cell rotation for specific values of current generated.

Data given in Fig. 18, shows the effect of the variation in ratio of radial positions of the two electrodes on the rotation rate required to achieve specific current (densities). For each current there is a



**Fig. 16.** Predicted and measured electrode potentials and cell voltage versus relative acceleration rate. The effect of KOH concentration and temperature on cell voltage as a function of relative acceleration rate. Anode and cathode: Ni foam. Temperature: 25 °C.



**Fig. 17.** Effect of rotation rate ( $\omega/s^{-1}$ ) on cell potential in a magnetic field (after Iwakura [158]).  $R_2 = 20$  cm.  $R_1 = 10$  cm. A: Predicted potential with rotation only B: predicted potential Magnetic field = 0.02 T.

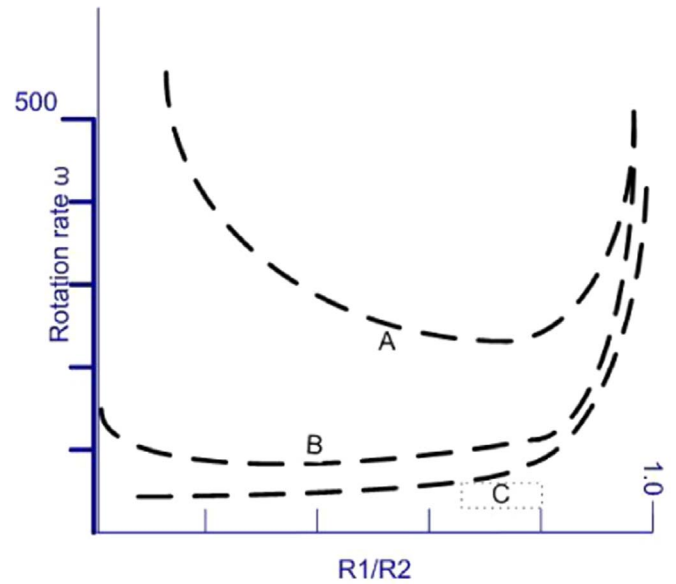
minimum rotation rate required at a specific radial distance ratio. This is because the Ohmic cell resistance decreases with decreasing distance between the electrodes; however, the area of cross-section of rotating cell also decreases (proportionally to  $(R_2^2 - R_1^2)$ ) and as a result, it becomes necessary to increase the rotational rate. Hence, for any conditions, an optimal geometry can be chosen to minimise the rotation rate of electrochemical cell. With increasing current, the geometric factor increases, i.e. the inter-electrode distance decreases and, correspondingly, the Ohmic resistance decreases.

The power to operate the electrochemical cell is the sum of that required to generate current for electrolysis ( $= EI$ ) with the associate internal resistance and electrode polarisation losses and that to overcome the frictional resistance to rotate the cell in air given by:

$$\text{Frictional loss} = M_f \omega. \quad (29)$$

Where  $M_f$  is the moment of friction force for the cell

The power is given by the following expression [161]:



**Fig. 18.** variation in the required rotation rate as a function of electrode radial position ratio ( $\ln(R_1/R_2)$ ), for specified current densities.  $H = 5$  cm.  $E = 1.3$  V. Outer diameter 50 cm. Electrolyte conductivity 0.05 S/cm.  $B = 1.0$  T. ( after Bograchev [161])  $R_1 = 25$  C = 1.25 mA/cm<sup>2</sup>, B: 12.5 mA/cm<sup>2</sup>, A: 125 mA/cm<sup>2</sup>.

$$W = I^2 \frac{\ln(R_2/R_1)}{2\pi\kappa_E H} + \eta_T I + 4\pi\eta/s \left[ \frac{\eta_T - I \ln(R_1/R_2)/(2\pi\kappa_E H)}{B(1 - (R_1/R_2)^2)} \right] \quad (30)$$

Previously Bockris [149] showed that the energy necessary to drive a homopolar generator could be calculated from an electromagnetic torque ( $T_{el}$ ). The power,  $P$  (in watts), is given by

$$P = T_{el} \omega, \quad (31)$$

where  $\omega$  is the angular velocity of the disc used (in rad/s) and where  $T_{el}$  is given by:

$$T_{el} = I B (R_2^2 - R_1^2)/2 \quad (32)$$

Note the similarity in the power needed for both devices even though the geometries are significantly different. Bockris's expression however ignores the power needed to overcome the frictional resistance of rotating the electrodes in the liquid electrolyte. Bockris estimated that the magnetic field required to rotate a 30 cm diameter electrode at 2000 rpm and to achieve electrolysis potential for hydrogen, was of the order of 0.9 T. This is a similar to the magnetic field estimated by Bograchev to achieve current densities of the order of 1.0–10 A/cm<sup>2</sup>.

Although the above calculations look attractive for possible practical applications there has not been substantial experimental data that support the work. The energetics related to electrochemical cells are well established and for example in chlorine cells there is a minimum amount of electrical energy (Gibbs energy) and thermal energy that is required; the latter of which can be derived from the internal Ohmic heating effect. Hence a rotating cell can be seen as an alternative device to provide that total energy facilitated by the magnetic field converting the rotational energy into electrochemical energy. The attraction of rotation is in the enhanced mass transfer and bubble disengagement with a resultant reduction in polarisation losses with only a potentially small sacrifice in power loss associated with cell rotation in air.

## 5. Light and photo-electrochemical processes

The use of light as a method to intensify electrochemical processes is primarily seen as a way of supplementing the electrical energy required for electrolysis based on photo-electrochemistry. Photo-electrochemistry involves the conversion of light energy into electrical energy (directly or indirectly via chemical transformations) using semiconductors [161]. The general behaviour of semiconductors is



determined by the energy level gap, where no electronic states exists, which separates the valence and conduction bands, which do have electronic states. The ease with which electrons in the semiconductor can be excited from the valence band to the conduction band depends on the energetic difference between these two bands; the size of which determines whether a material is a semiconductor or an insulator-nominally and this dividing line is around 4 eV. This band gap, can to a great extent determine the semiconductors optical absorption properties. There are two types of general semi-conductors called “n-type” an “p-type”. Current conduction in a semiconductor occurs via free electrons and “holes”, collectively known as charge carriers. Adding impurity atoms to a semiconducting material, known as “doping”, greatly increases the number of charge carriers within it. When a doped semiconductor contains excess holes it is called “p-type”, and when it contains excess free electrons it is known as “n-type”. In an “n-type” semiconductor, the movement of electrons in the conduction band carries the current.

Several useful processes (see Table 3) that harness light energy can be created by applying semiconductor photo-electrochemistry such as photocatalytic and photosynthetic processes [162]. In photocatalysis, using a suitable semiconductor, such as titanium dioxide, energy from the sun can be harnessed to produce highly reactive electron-hole pairs. When immersed in water, the semiconductor will establish a strong electric field at the interface between the solid and the liquid which separates electrons from holes and allows them to perform reactions. Water now in contact with the semiconductor can be oxidised by holes to hydroxyl radicals, which are powerful oxidizing agents. Additionally, excited (high energy) electrons can react with dissolved oxygen to produce superoxide radicals which then combine with  $H^+$  to form hydrogen peroxide. These species, produced by the electrons and holes, can for example degrade organic pollutants in the water and decontaminate water that contains harmful bacteria and viruses. A photosynthetic cell is a special case of the photocatalytic cell in which the chemical reaction that is created by solar energy produces a potential useful chemical or a fuel [163]. By using for example a strontium titanate electrode it is possible to use sunlight to drive water splitting redox reactions and thus store energy from the sun in the form of chemical fuel, i.e. hydrogen and oxygen as gases. By using the energy from excited (high energy) electrons generated in a semiconductor electrode in conjunction with appropriate catalysis, it is possible to reduce carbon dioxide into several different products, including: methane, methanol, formate and carbon monoxide.

Overall, photo-electrochemistry provides a route to store light energy directly in the form of chemical bonds without involving electricity as an intermediate energy carrier. This approach presents an opportunity for efficiency increases in the conversion process and for a reduction in the overall process cost. Both carbon dioxide reduction and water splitting can then provide clean and renewable energy. The main challenges in these applications is in producing cheap, abundant, and efficient light absorbers and catalysts, and integrating them into large scale systems. Other technical challenge for direct photo-electrochemical decomposition of water to occur include:

1. the semiconductor system must generate sufficient voltage to split water,
2. the energetics (band edges) of the semiconductor must overlap that of the hydrogen and oxygen redox reactions,
3. the semiconductor system must be stable in aqueous electrolytes,
4. charge transfer from the surface of the semiconductor must be fast enough to prevent corrosion and also to reduce energy losses due to overvoltage

## 6. The future for intensified electrochemical processes

The environment within an electrochemical cell places considerable

restrictions on how any process intensification strategy can be implemented. A governing feature is that with, for example, electrolysis, a major requirement is to minimise electrical energy input. This factor is controlled by several aspects and directly relates to the ionic conductivity of the electrolyte; regardless of whether it is liquid or solid. Essentially cell design is traditionally geared towards having small and sometimes approaching zero gap between electrodes to limit Ohmic voltage contributions. Scaling up electrochemistry for many synthesis applications means having very compact multi-cell stacks. Such stacks have restricted sizes of electrodes of a few square metres or less, due to practical constraints of electrode material fabrication and electrical conductivity. This can be challenging for the introduction of PI in cell stacks (see Table 3). For example, attempting to intensify electrochemical processes using ultrasound is difficult in terms of cell design due to the challenge of introducing the ultrasound into the limited space between electrodes. Thus applications are in niche areas or potentially in areas where “large” single cells can be employed.

The use of light via photo-electrochemistry has similar constraints as ultrasound in terms of the introduction of light, typically through the rear (backside) of the electrode through transparent electrodes. In addition there are issues with intermittent operation due to non-continuous solar light availability, which would involve dynamic operation of cells. This dynamic operation potentially would result in degradation of electrodes due to variations in electrode potential and/or current density. One potential area for cell development could be with fibre optics technology using embedded or coated capillary fibres to transmit light internally to electrode surfaces. Regardless of these issues there is still potential for commercial development in the area of photo-chemical splitting of water to hydrogen using renewable solar energy; especially with multi-junction cells.

The use of fluid flow to promote greater electrochemical reaction rates by increased mass transfer to surfaces is well known and commonly practiced in flow electrolyzers. Similarly rotating electrodes have been significantly researched in electro-synthesis, in metal deposition, in effluent treatment and in gas evolution reactions. However the approach has met with limited commercial success; although found applications in metal ion effluent treatment in the form of recovering the ions as metal powders at the surface of rotating cathodes. Scale-ability of the system is an issue as it does not lend itself to multi-electrode compact cell design, as in flat plate electrode stacks. In addition treating effluents with low ( $< \text{ppm}$ ) of metal ions incurs significant energy penalties, due to small mass transfer limited current densities (and thus treatment rates) that arise. We note that the energy required for rotation is current density independent, and as such as the current density falls its contribution to the overall energy used increases. Large rotating disc systems have similar operating constraints and as such have not achieved commercial success. We not of course the rotating disc (and ring disc) electrodes are a tried and tested electro-analytical tool used and sold world-wide for laboratory studies in electrochemistry and engineering.

Rotating solid electrodes in liquid electrolytes is known to incur frictional (shear) resistance and thus demand relatively large energy inputs. Alternatively it is possible to rotate the fluid flow or the complete cell and apply significant centrifugal (or centripetal) forces within the cell that disrupt or thin the hydrodynamic boundary and diffusion layers at the electrode surface. This effect has been well demonstrated in both gas evolution reactions and in gas consumption reactions in aqueous electrolytes. It holds significant promise to realise major savings in electrical energy input (up to 30%) in comparison to traditional flow cells. The use of this method is just emerging from the scale of application in laboratory centrifuges to a scale using more practical cell rotation. This requires good engineering to manifold and seal the fluid flow entry and exit through rotating shafts. Additionally cell design requires robust electrical connections to the rotating cell and electrodes therein. Importantly, in taking this approach, the energy required for cell rotation, even at high rotation (thousands of rpm) is

**Table 3**

Applications, advantages and dis-advantages of process intensification methods.

Technique	Applications	Advantages	Dis-advantages
Centrifugal force/High G	Electrochemical gas evolutions such as hydrogen oxygen and chlorine. Gas reduction and oxidation reactions and fuel cells. Organic electrosynthesis	Enhanced mass transport rate. Improved bubble release  from electrode. Reduced Ohmic and mass transport polarisation. Lower electrical energy input. Can be used in conjunction with magnetic fields Increased mass transport.	More complex electrolyser design. Cell maintenance requirement increased.  Cell sealing and electrical connection more complex. Energy required in cell rotation
Ultrasound/ sonoelectrochemistry	Electroplating, Electrodeposition, Electropolymerisation, Electrocoagulation, organic Electrosynthesis. Materials electrochemistry, Environmental electrochemistry, Electroanalytical chemistry.  Hydrogen energy and fuel cell technology	Increase in electrodeposition thickness Increased electrochemical rates, yields and efficiencies. Increased electrodeposition porosity and hardness. Increased gas removal rate. Increased electrode cleanliness and electrode surface activation. Reduced electrode overpotentials Suppression in electrode fouling. Direct conversion of light energy into chemical energy.	Lack of reproducibility. Scale-up and design aspects which have slowed development. Almost certainly the reason Lack of reactors that have been purpose built for sono-electrochemistry
Solar/light	Gas evolution from water decomposition  Electrochemical gas reduction, e.g. O <sub>2</sub> Environmental remediation Organic synthesis, e.g. from CO <sub>2</sub> reduction.	Use a renewable energy source. Reduction in activation energy	Restricted to intermittent operation.  Relatively low response to visible light. Low efficiencies. Band gap limitations. Scale-up and cell stacking issues, due to access to light. Depth of penetration of light. Photo-catalyst instability and degradation. More complex cell design to install magnets. Control of magnetic field may be complicated
Magnetic field/material	Fuel cells and redox batteries Electrodeposition Gas evolution  Anodic oxidations  Fuel cells  Surface patterning	Induce convection at surfaces Enhances electrochemical gas evolution Control of localised surface flow  Induce fluid motion in micro-channels Can induce electrolysis with High-G or fluid flow	Restricted effect by limited availability of high flux (Tesla) magnets. Induced electrolysis in conjunction with centrifugal/intensified flow is limited or not proven
Moving electrodes	Electrodeposition. Environmental remediation.  Inorganic and organic electrosynthesis. Fuel cells. Gas evolution.	Enhanced mass transport. Ability to deal with low reactant and ionic concentrations. Reduction in surface fouling of electrodes	Complicated cell design. Limited capability to stack cells.  Increased maintenance requirements. Relatively high energy input for rotation
Rotating flow	Gas evolution	Enhanced mass transport.  Potential to initiate electrolysis with simultaneous application of magnetic field.	High turbulence or high shear flow may be required. Relatively high pumping costs.  Ability to induce electrolysis with magnetic fields not proven.

very small and much smaller than that required to overcome fluid/solid frictional resistance with rotating electrodes in liquids. It is believed that one of the first applications of the approach would be in the generation of hydrogen.

An alternative approach which has not been significantly, if at all tested, is the use of rotational flow such as Dean flow [164]. Dean flow can, for example, be induced in a curved rectangular channel, in which the laminar Poiseuille flow is subjected to a centrifugal force and centripetal force. These forces disrupt the parabolic profile of the laminar flow and cause the maximum point of velocity to shift from the centre of the channel cross-section towards the concave wall of the channel. This wall could then be an electrode surface within a cell at which a sharp velocity gradient develops. Overall the strong pressure gradient between the concave and convex channel walls and the velocity gradients cause hydrodynamic instability and development of secondary, rotational flows and vortices, from the concave to the convex wall of the channel, known as Dean flow.

Magnetic fields in conjunction with electrical fields have been shown to induce flow on the small scale, in for example micro-channels. The use of the technique on a large scale is not likely to be practical considering the complexity of the system in comparison to basic pumping mechanisms.

Magnetic fields in conjunction with fluid motion has been clearly demonstrated to create electrical potentials between electrodes in a cell. This effect has the theoretical possibility of inducing electrochemical reactions at separated electrodes, for example, gas evolutions. The method will require significant energy input via the fluid motion force and may be aided by a thermal energy input from moderate heating or a waste heat source (or even possibly Ohmic heating from the cell). Importantly the magnitude of the magnetic field should be high, and several Tesla in value, to create a significant electric applied field that is capable of inducing electrolysis at practical and significant high rates. A critical factor with using magnetic fields will be to control the intensity and direction to best capitalise on the effect.

It goes without saying that fundamentally to induce electrolysis using external force fields, other than by direct applied electrical potential, requires and energy input at least equal to that required for the electrochemical reaction at a specific rate. Thus the few reports (with limited or no experimental data) and claims, which are mainly of a theoretical nature, for electrolysis via electro-hydrodynamic induction based on rotating cells or high velocity spiral flow, need to be experimentally validated. Such validation must, as well as show clearly an efficient conversion of total energy into electrochemical reaction, consider the overall energy transformation into electrochemical products. This will require good cell design in terms of fluid sealing and manifolding and electrical connection in the case of rotating cells or even electrolyzers.

In the field of fuel cells (and batteries) there has been limited research on the use of process intensification. In principle the limitations that arise in the case of electrolysis are similar to those that have been or would be experienced with fuel cells which convert chemical energy into electrical energy. The fuel cell related reaction of oxygen reduction has been intensified both with rotating cells and electrodes and with photo-electrochemistry. The benefits are seen as a reduction in overpotential losses, particularly linked to improved mass transport with the application of centrifugal forces in the cell. Magnetic materials have also been shown to benefit certain fuel cell reactions. However the application of PI in this area is largely under-researched and deserves further study in view of the potential energy benefits of higher power and efficiency. Controlling the force field and magnetic field and direction is crucial to the eventual exploitation.

## 7. Conclusions

Process intensification of electrochemical cells can be achieved using a range of methods which include the use of electrode rotation or cell rotation, ultrasound and magnetic fields. Cell rotation can lead to reductions in overpotential and Ohmic voltage losses associated with more effective gas bubble release. Superimposed magnetic field can significantly affect the water electrolysis process and IR-drop between the electrodes could be reduced and the fractional bubble coverage and a reduced bubble size have also been affected. The external magnetic field effects are due to the Lorentz-force-driven convection, i.e. the so-called magnetohydrodynamic (MHD) effect, which introduces additional convection in the electrolyte. A localised convection can also be induced close to a bubble due to a nonhomogeneous current distribution in the bubble vicinity; the so-called micro-MHD effect. The introduction of a magnetic field can decrease bubble coverage on a gas evolving electrode surface and also decrease the void fraction of dispersed bubbles in the electrolyte with a concomitant reduction in Ohmic voltage drop and overpotential and thus a reduction in cell voltage and an increase in energy efficiency; which of course must be balanced by the additional cost in applying a magnetic field.

MHD and redox MHD are capable of moving fluids along micro-channels, in the presence of an electrolyte, for applications in lab on a chip technologies. Redox-MHD microfluidics is also capable of inducing fluid rotation using on-chip concentric disc-ring microelectrodes, without the need for sidewalls or channels to guide the flow.

Progress in magneto-electrochemistry is being made through, studying the influence of the Lorentz force on convection at different length scales, and investigating non-uniform fields, and the Kelvin force. The Kelvin force can be very large at ferromagnetic microelectrodes and in the vicinity of nanostructured ferromagnetic arrays and there are opportunities for their use to study the diffuse layer and the double layer. Passive field-gradient electrodes can be used to modify electrode kinetics when paramagnetic species such as free radicals or molecular oxygen are involved. Magnetic field gradients have potential for patterning electrode deposits and controlling flow in electrochemical cells.

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