

Fuel cell electrolytes: evolution, properties and future prospects

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Abstract

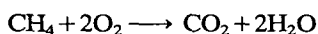
Any electrolyte with sufficient ionic conductivity may be used in a fuel cell, but to avoid concentration gradients in the electrolyte, active conduction should be via an ion produced in one electrode reaction and consumed in the other. This ion must be present at high concentration in the electrolyte. In aqueous fuel cells operating on hydrogen and oxygen, the only useful electrolytes have high concentrations of either H^+ or OH^- , i.e., strong acids or bases. The product of the anode reaction in aqueous acids, H^+ , occurs as a 'carrier ion' complexed by H_2O as $\text{H}(\text{H}_2\text{O})_n^+$, where n lies between 1 and 4. The corresponding cathodic product ion in bases, OH^- , is itself a 'carrier ion', the reaction product of O^{2-} (from the reduction of O_2) and H_2O . Phosphoric acid is not an aqueous acid, but a unique self-ionizing amphoteric system, in effect a molten acidic (H^+) salt. In molten salts, H^+ could be the primary conductor, e.g., in molten bisulfates. Less corrosive carbonate melts use a cathodic supply of CO_2 supplied via the gas phase to give CO_3^{2-} as the O^{2-} 'carrier ion'. A similar approach may be used in aqueous carbonates. No carrier material is needed in solid oxides, which conduct directly via O^{2-} ion. The temperature windows for different electrolytes are limited by performance at the low end and materials considerations at the high end. As a result, there are no electrolytes capable of operation between 480 and 900 K, and between 1050 and 1220 K. Development of electrolytes for these temperature ranges would be valuable.

Introduction

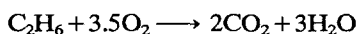
Fuel cells directly convert the Gibbs energy ('free energy') of fuel oxidation into work in the form of direct current electricity. They use a controlled electrochemical combination of reactants at constant temperature unlike the uncontrolled process which takes place when the fuel is burned to produce heat.

By definition, a true 'direct energy conversion' device is one which can directly convert one form of Gibbs energy into work. A photovoltaic cell accepts Gibbs energy in the form of a directed beam of photons and converts it to electrical work in the form of a directed stream of electrons under isothermal conditions. A fuel cell, a specialized form of a battery, directly converts the Gibbs energy of a chemical reaction into a directed stream of electrons under isothermal conditions. Like a photovoltaic cell, a practical operating fuel cell normally consumes no heat which eventually reappears as work. It is therefore not subject to the Carnot limitation, since Gibbs energy can in principle be converted at 100% efficiency. Practical efficiencies will be lower, and the systems will reject unconverted Gibbs energy in the form of heat. In theory, a perfectly reversible fuel cell operating with certain fuels and oxidants may be expected

to absorb heat from the surroundings and convert it into work if ΔS for the reaction is positive. The maximum amount of work which can be obtained from the isothermal electrochemical oxidation of a fuel at temperature T is $-\Delta G_T$. If the entropy of reaction, ΔS , is positive, then $-\Delta G$ will be numerically greater than $-\Delta H$. The reversible electrochemical cell should then operate endothermically. In general, oxidation reactions in which ΔS is significantly positive involve a net increase in the number of molecules in the gas phase on going from reactants to products. Whereas methane and ethylene oxidation:



have ΔS values which are close to zero if the product is gaseous water, those for higher paraffins and olefins will be positive, e.g.:



Similarly, ΔS for the oxidation of gaseous methanol and higher saturated alcohols to gaseous water will also be positive:



as is the oxidation of gaseous ammonia to gaseous water:



Another often quoted example is the oxidation of solid carbon to CO:



In all of the above, a reversible fuel cell operating with the above reactant and product states could, in principle, have a thermal efficiency greater than 100%. If liquid water is the product in reactions (2)–(5), then ΔS will be negative and the corresponding thermal efficiencies will be less than 100%.

Conditions for electrochemical direct energy conversion

To extract the Gibbs energy of reaction of two chemical compounds as electrical work, the compounds must react with each other isothermally. They must also react separately, i.e., unmixed. They must therefore react via a common medium, namely an electrolytic solution. In a throw-away alkaline battery, the common medium is KOH solution, which also serves as a reservoir for the water required as a reactant at the surface of the oxidant. The oxidant is MnO_2 . Because it is ionically conducting, the KOH solution allows the OH^- ion produced in the reduction of MnO_2 to flow to the reacting zinc at the negative electrode, where it is consumed. The zinc and MnO_2 will only react if an electronic pathway exists between them, so that electrons can be transferred from the oxidation of zinc to the reduction of MnO_2 . This occurs via the electronically conducting wire joining the two reactants.

Extraction of the Gibbs energy of reaction can therefore only occur if both reactants are separated by an ionically conducting medium which conducts via an ion produced in the electrochemical reaction at one of the electrode materials and consumed at the other. It also requires simultaneous collection of the electrons at the anodic

reactant and means of conducting them to the cathodic reactant. Finally, it requires separation of the pathways for both ionic and electronic conduction. If the ionically conducting medium is also an electronic conductor, no external work will be done, and ΔG will appear not as work, but as enthalpy resulting from an irreversible entropy change, i.e., $+T\Delta S_{\text{irrev}}$, where T is the ambient operating temperature. The same will happen if the electrodes are allowed to touch, short-circuiting the electronic pathway. The anode and cathode then show zero potential difference, so that all of the Gibbs energy of reaction is dissipated as enthalpy. The reaction conditions then are totally irreversible, as they are in a normal thermal chemical reaction. Under these conditions:

$$\Delta H = T\Delta S_{\text{irrev}} + T\Delta S \quad (6)$$

where ΔS is the reversible entropy of reaction. A complete separation of charges is provided by the totally ionic nature of the electrolyte, which can sustain a potential difference between the electrodes corresponding to all or part of the Gibbs energy of reaction. This is because the Helmholtz double layer of positive and negative ions in the electrolyte at the surface of each electrode is a capacitor which can sustain an electric field equal to about 10^8 V cm^{-1} . The field exists over the potential range within the window of electrochemical stability of the electrolyte, beyond which it would be oxidized or reduced.

Batteries use an electrolyte and external electronic conductors with the highest possible ionic conductivity to minimize losses under net current flow. The ionic pathway is therefore under short circuit, and the electronic pathway does work by being coupled to a device which maintains the potential difference between the electrodes. This may be an efficient electromagnetic device (i.e., an electric motor), which converts the directed flow of electrons into mechanical work. The electrodes themselves must also be made as electronically conducting as possible. If poorly conducting reactants serve directly as electrodes (e.g., the MnO_2 cathode in the above example) they must be mixed with a stable electronic conductor such as graphite.

Biological direct energy conversion

In principle, it is possible to invert the processes occurring in a battery by shorting the electronic pathway between the electrodes and substitute an ionic (electrolytic) pathway containing a potential gradient established by an ionic concentration gradient. If this contains a hypothetical device, which can convert an ionic concentration gradient into work at high efficiency, then the overall effect is similar to that in a battery. Man has not devised a satisfactory method of converting an ionic gradient into work. About 3.8 billion years ago, Nature opted to use the ionic gradient approach to create useful work in the natural equivalent of batteries (or more accurately fuel cells), the mitochondrion [1], the direct energy converter in the cells of living matter. Mitochondria have a shorted electronic circuit between the anodic and cathodic electrode sites and use the ionic proton gradient, created by a proton circuit, across a biological membrane for direct energy conversion. The proton gradient is used for the synthesis of adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and phosphate ion. The mitochondria are in effect batteries which oxidize a fuel ultimately derived from glucose, i.e., nicotinamide adenine dinucleotide phosphate (NADPH) to its oxidized form NADP at the anode. The mitochondrion reduces molecular oxygen at its cathodic sites, i.e.:

(i) anode:



(ii) cathode:



(iii) overall:



Part of the Gibbs energy of reaction of NADPH with O_2 is available as a proton gradient in the neutral dilute saline electrolyte. The proton gradient results from H^+ ions created in the anodic reaction together with the OH^- ions created in the cathode process. Phosphate ion can then condense with ADP and OH^- near the cathodic sites with the production of ATP and water. The Gibbs energy stored in the ATP can be used throughout the organism.

Fuel cells

The above discussion of the operation of primary batteries and natural mitochondria allows an introduction to the requirements for practical fuel cell electrolytes. Primary batteries contain consumable electrode materials. As these are respectively oxidized at the anode and reduced at the cathode, the electrode structure degrades and finally collapses, and the battery will cease to operate. A fuel cell has electrode structures and reaction sites which are designed to be as invariant as possible. They are arranged in such a way that an oxidizable material (a fuel) can be fed continuously as required to the anode. Similarly, a reducible material (an oxidant) can be continuously fed to the cathode. Finally, provision is needed to remove the reaction product as it is formed. Thus, a fuel cell is a primary battery which is capable of continued operation as long as an oxidizable fuel and an oxidant are supplied to it. The fuel plays the part of metallic zinc, and the oxidant the part of MnO_2 in the primary alkaline battery. Today's fuel cells are reviewed in ref. 2.

Fuel cells are generally designed to operate on hydrogen-containing fuels. For reasons to be explained, the fuel of choice for high-performance fuel cells is gaseous hydrogen, although there are certain exceptions. Because of its availability, the oxidant is almost invariably molecular oxygen. For terrestrial purposes, this is obtained from air without separation, whereas in space cryogenic oxygen is used. Systems operating on halogens as oxidants are infrequently encountered, but they are sometimes referred to as fuel cells. Electrochemical cells operating on an oxidizing metal at the anode (e.g., zinc, aluminum, sodium, lithium) with an oxygen cathode are also sometimes referred to as fuel cells, but they are more accurately metal/air batteries. They are usually primary (not-rechargeable) systems with the exception of those with zinc anodes, which can be recharged in certain aqueous electrolytes.

Reversible thermodynamics in fuel cells

Unfortunately, the reversible thermodynamic considerations given in the introduction are only of academic interest, for two reasons. First, the objective of a fuel cell is to convert as much of the fuel as possible to the product, the maximum amount

of work which may be derived from the fuel will be that corresponding to $-\Delta G$ after conversion, i.e., at the product exit of the fuel cell. There, $-\Delta G$ will be less negative than the value at reactant inlet, since the concentration of the reactant will have fallen and correspondingly that of the product will have risen. Thus, the maximum voltage E_{\max} which a fuel cell can develop under reversible conditions at real conversions is given by:

$$nFE_{\max} = -\Delta G = -\Delta G_T^0 + RT \ln C_r/(C_p)^m = -\Delta H_T^0 + T\Delta S_T^0 + RT \ln C_r/(C_p)^m \quad (10)$$

where n is the number of electrons exchanged per molecule of reactant, F the Faraday constant (96 485 J equivalent⁻¹), R the gas constant (J mole⁻¹ T⁻¹), $-\Delta G_T^0$, ΔH_T^0 , ΔS_T^0 (J, J, J T⁻¹, respectively) are the Gibbs energy, enthalpy, and entropy of reaction under standard concentration (activity) conditions at operating temperature T (K); C_r , C_p are the ratios of the concentrations (activities) of exciting reactant and product leaving the fuel cell reactor to those in the standard state, and m is the reaction order of product relative to that of the reactant. In complex process involving several product and reactant molecules, the $C_r/(C_p)^m$ term is replaced by the appropriate law of mass-action expression with its appropriate reaction orders. Taking a simple case with hydrogen fuel, the overall reaction is:



where $n=2$ for each molecule of hydrogen. If the fuel cell is such that the product water is gaseous, and exits from the anode side, $m=1$, and the effect of the concentration term on E_{\max} at 80% hydrogen conversion (utilization) is -22 mV at 373 K, -28 mV at 473 K, -55 mV at 923 K, and -76 mV at 1273 K. If oxygen in air is the oxidant at an assumed utilization of 20% in a co-flow configuration, a further $+RT \ln (C_{\text{ox}})^{0.5}$ term must be added, which is equal to -15 , -19 , -36 and -50 mV at the same respective temperatures. While ΔH_T^0 , ΔS_T^0 are not markedly temperature dependent, $-\Delta G_T^0$ falls markedly with rising temperature because of the effect of $+T\Delta S_T^0$. Thus, E_{\max} for this supposed operational case would be 1.127, 1.092, 0.922 and 0.783 V at 373, 473, 923 and 1273 K, respectively, compared with the 298 K standard state value of 1.229 V (with liquid water product, i.e., at a vapor pressure of 23.76 torr). Thermal efficiencies are usually expressed in terms of $-\Delta H_T^0$ at 298 K. The electrical equivalent of this term (i.e., $-\Delta H_T^0/nF$) is 1.254 V (lower heating value, LHV, i.e., with gaseous water as product). Thus, the maximum LHV efficiency of a fuel cell operating under the above temperature and utilization conditions would be 71.8, 69.6, 58.8 and 49.9% at 373, 473, 923 and 1273 K, respectively, after correction for the fact that only 80% of the fuel is converted. If one postulates greater hydrogen utilizations at 1273 K, the effects of the concentration term lead to further successive reductions of E_{\max} , which are eventually not compensated by higher conversion. Thus, the maximum LHV efficiencies are 53.0 and 52.8% at 90 and 95% utilization, respectively. Thus, even under theoretical reversible conditions, there would be a theoretical limit for the thermal system efficiency. We shall see that formation of product water in the fuel stream is common to all electrolytes except acids. For these, the same arguments would apply to the cathode exit stream with $n=4$ (for O_2) and $m=2$. In both cases, if liquid water is the product, i.e., if the exit stream is cooled and the product water condensed, the system might be removed from the above reversible thermodynamic restrictions since the fuel or oxidant may be recycled. Whether this is feasible depends on practical considerations such as heat-exchanger costs, heat losses and pumping requirements for recycle.

Irreversible losses

The second reason is the reversible considerations do not apply, because the assumption is made that reversibility applies, i.e., the system operates at zero net rate. A fuel cell operating with reactants and products whose rates of reaction on appropriate catalytic surfaces are sufficiently high to prevent interference from any competing electrochemical processes should give the local reversible thermodynamic potential ($-\Delta G$) at zero net rate. However, under conditions of net current flow, ohmic, diffusional and kinetic losses occur. Under these conditions, the measured values of the cell potential are always less than the reversible value, i.e., some of the available Gibbs energy is converted into irreversible enthalpy as $T\Delta S_{\text{irrev}}$.

Careful engineering can reduce ohmic and diffusional losses to a minimum under practical operating conditions. The major losses are then kinetic. Deviations from the reversible thermodynamic potential values are usually called overpotentials or overvoltages. Tafel's equation [3] was first demonstrated for a typical electrochemical reaction (cathodic hydrogen evolution from acid electrolytes). It can be written:

$$V = a + b \ln j_c = a + b \ln nFk \quad (12)$$

where V is the electrode potential, j_c the cathodic reaction rate expressed as a current density (A cm^{-2}), k the rate expressed in molecules $\text{cm}^{-2} \text{s}^{-1}$, n the number of electrons successively transferred per reacting molecule, and a and b are constants for a given reaction and substrate, at a given temperature. The constant b is generally proportional to T , and is equal to $-RT/\alpha_c F$ where α_c , the cathodic transfer coefficient, is a constant which depends on the reaction mechanism. The negative sign indicates that the cathodic current density increases as V decreases. In most cases, transfer coefficients lie between 0.5 and 1.5. In the anodic direction (hydrogen oxidation), the corresponding equation has constant a' and b' , where b' is equal to $RT/\alpha' F$. For cases which are commonly encountered:

$$\alpha_c = n' + \beta(n_{\text{rds}})$$

and

$$\alpha_a = n'' + (1 - \beta)(n_{\text{rds}}) \quad (13)$$

where α_a is the corresponding transfer coefficient, β is a dimensionless quantity called the symmetry factor, which is usually close to 0.5, n' is the number of electrons which are transferred in the reaction sequence before each single rate-determining step (rds) in the cathodic direction, in which (n_{rds}) electrons are transferred, and n'' is the number similarly transferred in the anodic direction. Only one electron is permitted to be transferred at a time, so (n_{rds}) can only be one (for an electrochemical rds) or zero (for a chemical rds). Thus, $\alpha_c + \alpha_a = n$, where n is the number of electrons transferred in the overall process per unit rds. This may or may not be the same as n in eqn. (10). The net electrode reaction is the sum of the anodic (positive current) and cathodic (negative current) processes. Equation (13) therefore may be written as:

$$j = j_a - j_c = [\exp(a/b) \exp(-V/b)] - [\exp(a'/b') \exp(-V/b')] \quad (14)$$

where j_a is the anodic current density, and j the net (experimental current density). By definition, at the reversible potential, $j=0$ and $j_a = j_c$. Thus, the current for the anodic and cathodic processes at the reversible potential is equal to $\exp[(a - a')/(b' - b)]$ or $\exp[(\alpha_c \alpha_a (a - a')/n)]$. This can be conveniently written as j_0 , the current at equilibrium or exchange current. Thus, if η is the overpotential measured from the equilibrium

potential, the net current at any overpotential η will be given by:

$$j = j_0 [\exp(\alpha_a F \eta / RT) - \exp(-\alpha_c F \eta / RT)] \quad (15)$$

This is the Butler–Volmer equation. For small values of η , it gives:

$$j = j_0 [(\alpha_a + \alpha_c) F \eta / RT] = j_0 (n F \eta / RT) \quad (16)$$

This expression will be accurate to within 2% for $\eta \approx 0.5 \alpha_c F \eta / RT \approx 0.5 \alpha_a F \eta / RT$, i.e., for $\eta = \pm 0.06$ V at 298 K (25 °C), or ± 0.2 V at 923 K (650 °C). Outside of the linear range, the $(d\eta/d \ln j)$ relationships for the individual anodic and cathodic reactions in eqn. (15), i.e., $RT/\alpha_a F$ and $-RT/\alpha_c F$, are known as the Tafel slopes. They are conventionally expressed in \log_{10} terms, in units of mV/decade of current density.

For a rapid reaction on an effective electrocatalyst, j_0 may be 3×10^{-3} A cm⁻² at 342 K (75 °C). This is approximately the case of the hydrogen/oxidation reaction in aqueous medium on platinum electrocatalysts. To maximize current density, fuel cell electrodes consist of high-surface area electrocatalysts dispersed to give the most effective area of contact. An electrode containing platinum electrocatalyst dispersed in 10–20% by weight on high-surface area carbon is typical, using platinum with a specific surface area of 100 m² g⁻¹. At a catalyst loading of 0.1 mg cm⁻², each geometrical cm² of electrode contains 100 cm² of catalyst, i.e., an effective j_0 value of 3×10^{-1} A cm⁻² for hydrogen oxidation. For $\alpha_a = \alpha_c = 0.5$, and $j = 0.5$ A cm⁻², $\eta \approx 0.075$ V, the electrode will function with a displacement of only 75 mV from the equilibrium potential. Unfortunately, hydrogen oxidation is the exception, rather than the rule. Methanol is one of the most reactive organic compounds, but its j_0 value is at least 3 orders of magnitude less than that of hydrogen. Thus, at 0.5 A cm⁻², a high-surface-area catalytic methanol electrode may be displaced to 400 mV positive to the hydrogen potential. More reduced organic fuels, e.g., olefins, have even lower rates on the best dispersed catalysts [4], and methane shows no perceptible oxidation at all below 1000 K.

The cathodic reduction of dioxygen molecules proceeds poorly in aqueous media, even on the best noble metal catalysts. Reaction rates are typically 10⁻⁶ times lower than those for hydrogen oxidation in the same medium and at the same temperature in the range 373–473 K. The reasons for this have been reviewed in refs. 5 and 6. Because of the Tafel law, oxygen cathodes only operate at about 0.75–0.80 V versus hydrogen at 0.5 A cm⁻² on effective electrocatalysts in aqueous acid media and at about 0.85 V under the same conditions in alkali. This results from a lower Tafel slope due to a change in mechanism at high pH [6]. Because the cathodic reaction is so irreversible in these media at usual operating temperatures, any reversible thermodynamic calculations at the cathode do not apply. The cell potential is essentially determined by irreversible cathode kinetics and may be at about 0.7 V at 0.5 A cm⁻².

Because reaction rates increase with temperature, the oxygen electrode correspondingly improves as temperatures increase. This means that noble metal catalysts can be replaced in most cases by other stable materials. At the same time, the stabilized specific areas of available electrocatalysts are reduced as sintering rates increase. This means that oxygen-reduction rates per unit of geometric metric area may not improve as would be anticipated with increasing temperature on porous electrodes. At sufficiently high temperatures, the oxygen electrode will eventually become rapid enough to approach reversibility, behaving like the hydrogen electrode on high-surface-area platinum at low temperatures in acid media. However, as temperatures rise, E_{\max} falls, which largely compensates for increasing reversibility of the oxygen cathode. As a

result, a fuel cell operating at 923 or 1273 K will still be in the 0.65–0.73 V range at practical current densities, the same as a phosphoric acid fuel cell operating at about 473 K.

Carbon-containing fuels

A practical fuel cell must be aimed at using practical primary energy. This means common carbonaceous fuels. The hydrogen electrode is reversible on noble metal catalysts in aqueous electrolytes. Because of the losses at the oxygen electrodes, aqueous systems operate on hydrogen at about 0.7 V, i.e., at about 56% LHV efficiency. The high reactivity, i.e., exchange current, of hydrogen is unfortunately the exception, rather than the rule. Other hydrogen-containing fuels, with the exception of hydrazine and hydroxylamine, show much lower rates of reaction.

Carbon-containing fuels with the highest electrochemical activity are those which are partially oxidized and contain one carbon atom, i.e., formic acid (HCOOH, two-electron oxidation, -1.480 eV), formaldehyde (HCHO, four-electron oxidation, -1.350 eV) and methanol (CH₃OH, six-electron oxidation, -1.214 eV). The values are $-\Delta G_{298}^0$ for the combustion reaction, expressed in electron-volts (volt-faradays per equivalent). For toxicological reasons and because the enthalpy of combustion per unit mass falls dramatically as the degree of oxidation increases, only methanol has been seriously considered as a fuel.

The electrochemical oxidation of methanol and other oxidized carbon species in aqueous media has been widely studied [7, 8]. The most effective electrocatalysts are platinum alloys, for example with tin and ruthenium. After adsorption, dissociation of C–H bonds takes place on platinum. This is followed by oxidation of the adsorbed hydrogen. Partial oxidation of the carbon then occurs via OH species, derived from partial oxidation of water molecules adsorbed on the electrocatalyst surface, which are associated with less noble alloying metals. Finally, an adsorbed CO group remains, identical with that formed if CO is present during the electrooxidation of gaseous hydrogen which acts as a catalyst poison. The reaction is self-poisoning, and the CO group can only be eliminated by exposing the electrocatalyst to high positive potentials of about $+0.83$ V versus hydrogen. Even with liquid methanol at high concentration, the oxidation process has a j_0 value about 10^{-4} times less than that of gaseous hydrogen oxidation. For hydrocarbons and compounds with fully reduced carbons, reaction rates are orders of magnitude less. Methane is totally inert even at 200 °C in aqueous media (concentrated phosphoric acid). Direct methanol cells are still of some interest but their low cell potential (i.e., low thermal efficiency), generally low current density, requirement for high catalyst loading, and the general tendency for unreacted methanol to diffuse through the electrolyte and affect the performance of the oxygen cathode have limited their application.

Since reaction rates increase with temperature, the question arises as to whether yet higher temperatures will give useful reaction rates for carbonaceous fuels. With appropriate catalysts, they react with steam to produce H₂ and CO/CO₂ mixtures, depending on the temperature, CO₂ being favored at low temperatures. As temperatures of 523 to 573 K and beyond, methanol will steam reform readily via this reaction. Hydrocarbons fed directly to high temperature fuel cells (HTFCs), e.g., the molten carbonate (MCFC) system at 923 K, may show some tendency to oxidize but they also decompose by cracking, producing carbon deposits. One effective way of eliminating cracking is the injection of steam with the hydrocarbon to shift the equilibrium:



towards the right. This results in an environment in which the hydrocarbon itself is likely to steam reform, e.g., for methane:



The hydrogen formed is oxidized much more rapidly than either methane and CO, so it is rapidly consumed to produce more steam. The CO undergoes the rapid exothermic water-gas-shift reaction with excess steam to produce more hydrogen:



If internal reforming is used, at first sight methane is oxidized directly. In effect, it decomposed to CO_2 and H_2 in the gas phase, and only the latter is oxidized at the electrode surfaces. For methane, the steam-reforming reaction normally takes place at high rates only at about 800 °C on suitable catalysts. However, at 923 K, with the same catalysts, its rates are sufficient to maintain the reactions on fuel cell electrodes. While methanol requires a much lower reforming temperature, ethanol and other compounds containing fully reduced carbon atoms require high temperatures.

Hydrogen fuel

All of today's fuel cells, therefore, effectively operate on hydrogen as the fuel, whether pure (if available or necessary, for example in space) or on mixtures of hydrogen and carbon dioxide produced from common fuels. Fuel cells operating at high temperature can be designed to reform methane (natural gas) directly using waste heat. Thus, they act as thermodynamic 'black boxes' which appear to operate on methane ($-\Delta H_{298}^0 = 1.040$ V, LHV). Thus, a fuel cell operating at 0.7 V on methane at 85% utilization would have a d.c. LHV efficiency of $(0.7 \times 0.85)/1.040$ or 57.2%. Fuel cells operating at low temperature require external steam reforming of the fuel feedstock (typical impure methane, i.e., natural gas), followed by water-gas shifting to reduce the CO content of the H_2/CO_2 product to acceptable levels. For acid fuel cells operating at 473 K, this level is less 1.5% CO by volume to avoid poisoning at near the anode exit, where hydrogen concentrations are low. At 373 K, the limiting concentration would be a few ppmv.

Aqueous electrolytes for hydrogen-oxygen fuel cells

Reactions and ion transport

In an aqueous hydrogen oxygen fuel cell, possible electrode reactions might be:

(i) anode:



(ii) cathode:



(iii) overall:



It can be seen that these are the same as the reactions in a mitochondrion, except for the lack of the NADP hydrogen carrier. However, the mitochondrion operates in a dilute physiological electrolyte with a mean pH of about 7. This contains very small residual amounts of H^+ or OH^- ions, which are overwhelmed by their rates of production at the anodic and cathodic sites. The mitochondrion also uses a semipermeable membrane to maintain the pH gradient to do chemical work. The electronic current is short-circuited through the membrane via Nature's equivalent of copper wire, a series of successive embedded redox couples which permit the passage of electrons from the anodic to the cathodic sites.

In contrast, a man-made fuel cell must perform all work in the external electronic circuit, and hence it must minimize the voltage losses in the ionic circuit. Above all, it must avoid any concentration gradient for ions formed (or consumed) in the electrode processes, since these result in an irreversible change in the effective Gibbs energy of reaction. To avoid concentration losses, the fuel cell must use an electrolyte whose majority conductor is the ion produced in the reaction at one electrode and consumed at the other. This ion must carry all of the charge during operation, so its transport number must be as high as possible. An electrolyte for a high-power-density aqueous fuel cell must therefore be a concentrated solution containing this ion, which should be the exclusive anion or cation in the electrolyte.

For example, if we take a hypothetical case where H_2 and Cl_2 are the fuel and oxidant, this ion may be either H^+ or Cl^- . Thus, an acidic electrolyte or a concentrated chloride solution (or a chloride melt) may be used. If H_2 and O_2 are to be used, the ion can be either H^+ or O^{2-} , or derivatives of these ions. Thus, the electrolyte may generally be an acid, an oxide, or media containing 'carrier ions' for either H^+ or O^{2-} .

Whereas mitochondria function on the pH change represented by concentration gradients in dilute neutral solutions, a practical fuel cell operating at economically effective current densities requires a strongly acid or strongly alkaline electrolyte to function effectively. Under these conditions, the cell reactions will be:

(i) anode, acid electrolyte:



(ii) cathode, acid electrolyte:



(iii) anode, alkaline electrolyte:



(iv) cathode, alkaline electrolyte:



Alkaline fuel cell electrolytes

In an alkaline fuel cell (AFC), ionic conduction is via OH^- ions produced at the cathode. These are carrier ions for O^{2-} formed by reaction of this species with one water molecule. The O^{2-} ion may be transiently present as a cathodic reaction intermediate, depending on the electrode reaction mechanism. After conducting the ionic current from the cathode to the anode, OH^- effectively reacts with H^+ (reaction (25)) producing water, which is rejected at the anode. We must stress that alkaline

electrolytes require pure hydrogen or hydrogen gas mixtures from which CO_2 has been removed, otherwise the electrolyte is rapidly carbonated. This removes the conducting ion, so that the cell ceases to operate. The only cost-effective aqueous alkaline electrolyte is concentrated aqueous KOH solution (about 8 N concentration or greater, depending on operating temperature). Potassium carbonate is about four times more soluble than sodium carbonate at typical cell-operating temperatures, so it is less likely to be affected by carbonate precipitation. Cesium or (preferably) rubidium hydroxides would be perhaps preferable, but their use is not cost-effective.

Aqueous acid electrolytes

In aqueous acids, the active ion produced at the anode reaction is H^+ . In the cell, this occurs as a carrier ion complexed by H_2O as $\text{H}(\text{H}_2\text{O})_n^+$, where n lies between 1 and 4. Conduction in the cell is via protons, hopping between $\text{H}(\text{H}_2\text{O})_n^+$ and correctly oriented adjacent water molecules by quantum-mechanical tunnelling [9]. At the cathode, protons react with dioxygen in the overall process shown in reaction (25), and water is produced at the cathode. We should note that the aqueous proton-conduction mechanism described in ref. 9 does not require the transport of water molecules from the anode to the cathode.

Early AFC work used sulfuric acid. This could only be operated up to about 80 to 90 °C, since it was reduced at the hydrogen anode. A search for other possible acids showed that only phosphoric acid had both the required stability and low volatility to operate at higher temperatures [2, 10]. The original objective of this work was the development of a direct hydrocarbon fuel cell operating at 423 K or higher. Performance was however very poor and catalyst requirements were excessive [10], which led to this approach being abandoned. Since phosphoric acid operating under these temperature conditions is not an aqueous acid, it is discussed in a separate section.

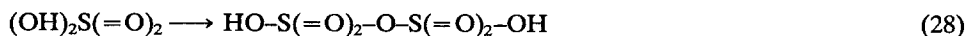
In parallel to work on the direct hydrocarbon phosphoric acid fuel cell (PAFC) system, the General Electric Company developed another acid system for application as a power source for the Gemini space capsule, in which its product water could also be used for drinking. The system had to be simple and light, because of the weight constraints of the small space capsule. The system was called the Solid Polymer Electrolyte system (SPE[®]) by its developer, and used a solid sulfonic acid electrolyte based on a non-fluorinated poly(styrene)-divinylbenzene copolymer backbone ion-exchange membrane. Water dissolved in the material but it was not itself soluble in water, so that product water was rejected automatically in pure form [10]. This cell was the forerunner of today's proton-exchange membrane (PEM) fuel cell, which uses a fully fluorinated sulfonic acid polymer for highest stability and acid strength.

Apart from the special case of phosphoric acid, no inorganic acids have suitable properties for use in fuel cells at temperatures approaching the boiling point of water. Possible candidates are either not strong, i.e., not sufficiently conducting (e.g., H_3BO_3 , $\text{H}_2\text{Si}_2\text{O}_5$, $\text{H}_2\text{W}_2\text{O}_7$, H_2UO_4), are too volatile (e.g. HCl), or decompose (e.g., H_2SO_4 , HClO_4 , HBF_4). After a number of attempts to use fluorinated organic sulfonic acids in aqueous solution [11], it was perceived that these had no real advantages over fluoropolymer sulfonic acid PEM material. In consequence, this is the only aqueous fuel cell electrolyte in use today.

Phosphoric acid

Orthophosphoric acid is not normally considered to be a strong acid, but at temperatures beyond the boiling point of water it becomes successively dehydrated

forming pyrophosphate polymer chains. Phosphoric acid is not an aqueous acid, but a unique self-ionizing amphoteric system, in effect a molten acidic (H^+) salt. Sulfuric acid (a relatively strong acid) shows the same property to a lesser degree, since it can dimerize to form pyrosulfuric acid. Their structures are as follows:



Orthophosphoric acid, H_3PO_4 , can self ionize to give $H_4PO_4^+$ and $H_2PO_4^-$. The corresponding ions in pyrophosphate chains will be $-O-P(OH)_2^+-O$ and $-O-P(O)_2^- -O$. Presumably protons can run along the chains giving high conductivity even at 200 °C; when the water vapor pressure over the hygroscopic polymer approaches 0.2 bar, the pressure at which product water vapor is rejected at the fuel cell cathode when the oxygen utilization in air feedstock is 50%. This property gives easy management of water vapor pressure.

Alternatives to phosphoric acid

Phosphoric acid was a useful electrolyte because of its ease of water management at operating temperatures approaching 473 K when its concentration (expressed as H_3PO_4) was about 97 wt.%. As the only available acid electrolyte for this temperature, it could directly operate on water-gas-shifted reformat. A fuel cell operating at this temperature could also supply waste heat for raising medium-pressure steam for reforming, which reduces LHV energy input by 13.2% at a steam-to-carbon ratio of 3. This is instrumental in raising the LHV system efficiency from 40 to 46%. The cathode performance of PAFCs is inferior to that of sulfuric acid and particularly, trifluoromethane sulfonic acid, CF_3SO_3H , under comparable operational conditions [11]. This acid became available in commercial quantities in 1970 and was shown to possess high stability. It was not suitable for use with normal high-surface-area electrodes bonded with polytetrafluoroethylene (PTFE, Teflon[®]), since the CF_3- group wets this material at high concentration, and the acid proved to be too volatile. It could be dehydrated to form a stable monohydrate, $CF_3SO_3^- \cdot H_3O^+$, which shows low proton mobility and conductivity.

An alternative electrolyte, $(CF_2SO_3H)_2$ was synthesized in 1979 [12]. It proved to be a stable, low-volatility material with excellent oxygen-reduction kinetics which did not wet PTFE because it lacked CF_3- groups. However, it proved to have little affinity for water at temperatures over 373 K, and its conductivity fell dramatically as it lost water to form a stable dihydrate [11]. A phosphonic acid analog, $(CF_2PO_3H_2)_2$ was also synthesized in 1980 [12], and was tested as a fuel cell electrolyte at 473 K to see if it showed the same conductivity properties as phosphoric acid. It also proved to become essentially non-conducting at this temperature at water vapor pressures in the range found in an operating fuel cell [13]. It clearly did not form polymer chains of the same type as phosphoric acid. Indeed, if it does, such chains would not be acidic, since the acid contains an insufficient number of protons. It can perhaps internally cyclize. It is much stronger than phosphoric acid, which will inhibit any possibility of protonation to give a cation. After some hours in the fuel cell, it appeared to decompose to phosphoric acid [13]. This work has been confirmed more recently [14]. Other exotic acids studied have been based on disulfone carbanions and disulfone imides, with the parent compounds $CF_3SO_2CH_2SO_2CF_3$ and $CF_3SO_2NHSO_2CF_3$, respectively [15]. In these, the $-NH-$ and $-CH_2-$ are strong acids, due to the electron-

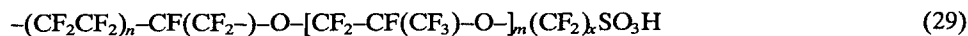
withdrawing action of the $-\text{SO}_2-$ and fluorinated groups. Like $\text{CF}_3\text{SO}_3\text{H}$, any compounds with terminal end groups wetted PTFE at high concentration. The parent compounds had rather high volatility, but they did increase the rate of oxygen reduction when added to phosphoric acid in small amounts [16]. Polymeric compounds of low volatility were thought to possess resonant structures which might have allowed proton conductivity along the chains. Polymeric perfluorinated disulfone carbanion acids could not be synthesized [17]. Synthesis [17] and testing [18] of their imide analogs showed that they became non-conducting at a vapor pressure of 0.2 bar above 373 K. Thus, like substituted sulfonic and phosphonic acids, they behave like normal aqueous acids.

The high-temperature conductivity of phosphoric acid therefore appears to be unique and it is associated with its amphoteric nature, i.e., the fact that it can form both anions and cations. This, in turn, is associated with its relatively weakly ionizing nature. The ability to be protonated is not to confer conductivity, as is shown by the fact that $\text{CF}_3\text{SO}_3^- \cdot \text{H}_3\text{O}^+$, which is fully ionized, is very poorly conductive. The medium must contain neutral molecules which can be protonated to allow mobility. In aqueous acids, this function is performed by water molecules, and in phosphoric acid by unionized molecules of the relatively weak acid H_3PO_4 . As the temperature and acid concentration increase, the conductivity of phosphoric acid rises. This reflects chain formation which results in the formation of pyrophosphate chains, which are not only stronger acids, but are able to enhance proton transfer along the polymer chains.

As a result, a substitute for phosphoric acid appears to be unlikely.

The PEM system

The early polymer electrolyte used in the Gemini fuel cell was much less stable than the later fluorinated materials typified by Nafion[®], a product of E. I. DuPont de Nemours and Company developed as a sodium-conducting membrane to produce pure NaOH for the chlor-alkali industry. The material was first synthesized in 1962 and was experimentally applied to use in the chlor-alkali industry in 1964, eventually replacing the mercury cell which posed environmental problems. Its first experimental use as a fuel cell electrolyte was in 1966 at General Electric. Fluorination made Nafion[®] not only more stable than sulfonated poly(styrene)-divinylbenzene sulfonic acid, but it also had much lower ionic resistance and higher performance. The fluorinated backbone of Nafion[®] contains the same elements as a combination of the Teflons[®] PTFE (polytetrafluoroethylene), FEP (perfluoroethylene-perfluoropropylene copolymer) and PFA (perfluoroalkoxy), i.e.:



where n is normally 2 to 3, $m=1$ and $x=2$. The material is a relatively dilute acid with about the same conductivity as 1 M sulfuric acid. It behaves as a typical aqueous acid from the viewpoint of conductivity, so that its use is limited to temperatures below the boiling point of water. Work at General Electric showed cells using Nafion[®] to be capable of attaining ten times the current density of the Gemini fuel cell under comparable conditions, provided that the cathodes were improved by adding Teflon[®] to provide a surface to avoid flooding by liquid product water. When General Electric sold its Nafion[®]-based technology to the Hamilton Standard Division of United Technologies Corporation in 1984, the successor company retained all rights to the SPE[®] trademark. In consequence, the technology is now known elsewhere as the PEM. Essentially pin-hole-free films of Nafion[®] are made from the acid fluoride precursor,

known as XR resin, which is the hydrolyzed form. The method of synthesis is described in ref. 19. The latest version from DuPont is Nafion[®] 105, which has similar ionic properties to materials from the Dow Chemical Company (for which $m=0$ and $x=2$) and the material known as Aciplex-S from the Asahi Chemical Industry Company, in which $m=0-2$, and $x=2-5$. The materials are made using slightly different chemistry and have slightly different properties, with equivalent weights of 1000, 800 and 1000, respectively. Typical film thicknesses are in the 125 μm range, resulting in cells with resistances of about 0.1 $\Omega\text{ cm}^{-2}$ or less when operating at temperatures below the boiling point of water under the particular imposed pressure conditions. Most groups report that external recycle of water is required from the anode to the cathode of the PEM, presumably to form the carrier ion. If this is true, it implies a mechanism of proton conduction which is different to that conventionally accepted in aqueous electrolytes where no net transfer of water molecules is assumed [9].

'State-of-the-art' performance from developers is 1.0 A cm^{-2} at 0.6 V on hydrogen and air at about 3 bar using electrodes with 4 mg cm^{-2} platinum loading. Since the parasitic work for air compression (including recovery of energy using an expander) is about 20% of fuel cell output or 0.12 V, this is equivalent to 38.3% LHV efficiency (32.4% HHV) assuming 100% hydrogen utilization. If pure hydrogen is used, close to 100% utilization is possible, since PEMFCs produce product water on the cathode side, and they can be fed hydrogen dead-headed at the anode, with allowance for an occasional purge to remove any accumulated impurities. The use of reformat from methanol (HHV for liquid methanol, 1.255 eV, LHV 1.103 eV, LHV for gaseous methanol, 1.171 eV) requires 0.083 eV for the heat of reforming, i.e., 6.6% of the heating value of the hydrogen produced. This may be provided by operating the 75% hydrogen/25% CO_2 reformat fuel at 90% anode utilization, and utilizing the anode off-gas in a catalytic reformer burner. At a steam-to-carbon ratio of 1.5, 0.173 eV is required to evaporate the water-methanol reformer feedstock. Thus, at an effective 0.48 V cell voltage and 90% utilization, the LHV efficiency of the system, assuming no other losses, is only 30.3%. Taking into account the efficiency of methanol manufacture from natural gas (about 67% LHV), this results in an overall steady-state efficiency of a PEM vehicle system about equal to that of an internal combustion engine operating under steady-state conditions. A further problem with the PEM is poisoning from traces of CO in reformat. Recent work at Los Alamos National Laboratory shows that removal of CO to below shift equilibrium levels, e.g., by partial oxidation or even methanation, may be thwarted by reverse water-gas shift of reformat, i.e. the formation of a few ppmv of CO from CO_2 and H_2 on the anode catalyst, which causes poisoning.

The secret of using PEM film electrolytes lies in the method of bonding of electrodes to the surface, to give the greatest effective three-phase electrolyte-electrocatalyst-gas phase boundary, making the best possible use of the electro-catalyst. Today, optimized interfaces can achieve 0.6 V at 0.5 A cm^{-2} and 0.7 V at 0.3 A cm^{-2} at atmospheric pressure using carbon-supported platinum cathodes with 0.1 mg cm^{-2} loading, and anodes with a loading of 0.05 mg cm^{-2} or less. Using 0.7 V as the nominal mean power point, the LHV fuel cell efficiency on pure hydrogen would be 55.8% at 100% utilization. The Rolls-Royce and Associates Ltd. autothermal reformer reported at the Third Grove Symposium [20] has a natural gas to reformat HHV efficiency of 91% (85.7% LHV). We can assume an advanced reformer with a conventional burner with an integrated shift converter with the same efficiency (e.g., in a system of flat-plate type, [21]) to produce a 80% H_2 /20% CO_2 mixture. The latest data for the work requirements to separate CO_2 using pressure-swing adsorption indicate a maximum of 0.35 kWh/Nm^3 [22]. If this is produced from natural gas at a modest

38% LHV efficiency, this will produce hydrogen from natural gas at 78.7% LHV efficiency. Assuming 5% compression loss, a hydrogen-fueled vehicle would operate from natural gas at 42% LHV efficiency with an atmospheric pressure fuel cell, twice the overall efficiency of a system operating pressurized on methanol. This will provide an effective way of reducing 'greenhouse'-gas emissions in the transportation field.

Molten salt electrolytes

In molten salt electrolytes, the rule that the majority charge carrier should be an ion produced at one electrode and consumed at the other requires the ions to be H^+ (in a molten proton-conductor), OH^- (in a molten hydroxide), or O^{2-} (in a molten oxide). The O^{2-} ion is produced in the simple four-electron charge-transfer process in the reduction of molecular oxygen. Molten proton-conductors such as acid salts, e.g., sodium bisulfate, are corrosive and often not stable, so they have not been widely examined as electrolytes.

Molten alkaline hydroxides are also corrosive, and suitable molten oxides only exist at temperatures which are beyond the capabilities of economic fuel cell construction materials. The Apollo fuel cell was a cell of Bacon [23, 24] type, operating on molten KOH pellets containing some residual water at about 533 K. Because alkali metal hydroxides react with CO_2 to give solid carbonates at cell operating temperatures, such electrolytes cannot be used with reformat. In consequence, the only molten salt electrolyte which has found application is a mixture of molten alkali carbonates, usually Li-K, with Li-Na being occasionally suggested. A eutectic or off-eutectic mixture is used to lower the melting point and to give improved transport and other physical and electrochemical properties, for example 62/38 Li/K or 70/30 Li/K. This is retained in a matrix of $LiAlO_2$ powder by capillary action with pore sizes in the matrix and electrodes adjusted to give correct filling. In the molten carbonate fuel cell (MCFC), oxide ion (O^{2-}) carries the current from anode to cathode in the form of a carrier ion, CO_3^{2-} . This is formed by supplying CO_2 along with O_2 as a reactant at the cathode:



The reaction with hydrogen at the anode is:



The CO_2 in the anode exit gas stream is then collected and recycled to the cathode gas. In this way, the overall cell process is reaction [11]. The use of CO_2 as a depolarizer in this manner eliminates the possibility of concentration gradients. In principle, other oxyanions could be used in this way, but they involve the use of non-gaseous or low-volatility oxides (e.g., SiO_2 , B_2O_3 or P_2O_5) or oxides with limited stability (e.g., SO_3 , which is reduced under anodic conditions). Thus, carbonates appear to be the only choice for a system based on the use of hydrogen-containing fuels and oxygen in molten electrolytic media. In addition carbonates show good stability in regard to oxidation and reduction and are generally non-aggressive in regard to corrosion behavior. Molten carbonate fuel cells have been reviewed in ref. 25. A similar approach using a CO_2 -depolarized cathode with anode-to-cathode CO_2 recycle has been used in aqueous carbonate electrolytes [26]. This approach combines a CO_2 -rejecting electrolyte with the advantage of cathode performance similar to that in alkaline electrolyte, even though CO_2 addition inevitably reduces O_2 partial pressure and complicates the oxygen reaction sequence.

In contrast to acid–electrolyte fuel cells, the HTFCs can handle CO, since it is spontaneously converted inside the anode chamber of the cell to H₂ and CO₂, via the water–gas-shift process. We have already remarked that the HTFCs (MCFC and SOFC) rely on O²⁻ transport from the cathode to the anode, either alone or via CO₃²⁻ as a carrier ion. Thus, water vapor is produced at the anode as H₂ is oxidized, which drives the water–gas-shift reaction and consuming any CO which is present until equilibrium is reached. As hydrogen is consumed across the face of the fuel cell anode, the fuel gas becomes more and more dilute, resulting in a fall in current density.

As with acid cells operating on reformat, it is therefore not possible to drive the reaction to zero hydrogen content in the fuel gas stream, unless some cost- and energy-economic method of gas separation could be devised. Hydrogen utilization in the MCFC is determined by economic considerations. The least costly way of recycling CO₂ from the anode exit stream to the cathode is by combusting with fresh process air. The enthalpy content in the stream may be used in an external reformer, or may be used for air preheating. Cooling the stream to condense product water, followed by heat-exchange to cathode inlet temperature does increase O₂ and CO₂ concentrations, thereby increasing cathode performance. However, this is generally not feasible, due to the high capital cost of heat-exchangers. In consequence, the cathode in a real system is forced to operate at about 10% CO₂/12% O₂, and the anode exit stream is not allowed to exceed 75% utilization to allow sufficient enthalpy for air preheating by direct mixing, thereby eliminating a further heat-exchanger for air preheating. Today's developers (Energy Research Corporation) have succeeded in operating atmospheric pressure systems on indirectly internally-reformed natural gas at 0.746 V at 160 mA cm⁻² (0.72 V at 200 mA cm⁻²) under these conditions, in a cross-flow cell with a polarization slope of about 1.3 Ω cm⁻². Both the anode and the cathode show reversible behavior with about 15% of the polarization at the anode, the remainder being approximately evenly split between IR drop and cathode polarization. The power density of the MCFC is therefore rather low, which involves a materials cost penalty, since sintered nickel anodes, lithiated nickel oxide cathodes formed from nickel sinter plaques, a stainless-steel cathode current collector, and a ribbed stainless-steel bipolar plate nickel-clad on the anode side are required in a cell with a substantial mass of material per kW. However, one advantage of operation in dilute CO₂ cathode gas at atmospheric pressure is that it minimizes dissolution of the nickel oxide cathode with ultimate precipitation of metallic nickel near the anode, and reduced cell life.

Solid oxide systems

While molten oxides are not feasible as electrolytes, at sufficiently high temperatures, certain ionically doped oxides become effective O²⁻ ion conductors. Thus, they may be used as electrolytes in the solid oxide fuel cell (SOFC) operating on hydrogen-containing fuel and oxygen. This is advantageous, since the cathode can operate directly on process air, which is used for cooling at low utilization, so that losses due to low oxygen partial pressure are minimized compared with the MCFC. The only practical solid oxide electrolyte is yttria-stabilized cubic zirconia (YSZ, 8% yttria), which is sufficiently conductive in thin layers at temperatures of 1073 K and above. Since it is a ceramic, it must be matched with other components of matched coefficient of expansion, e.g., porous lanthanum strontium manganite as the cathode and nickel oxide–YSZ as the anode, which is reduced to Ni–YSZ cermet in operation. The methods of fabrication of porous electrode layers on dense electrolyte, with means of current collection and separation of reactant gases, have been solved (or partially

solved) by different developers using different approaches. Some of these have been reviewed [27]. Some developers in Japan are experimenting with the use of the much tougher, though somewhat less conductive, partially stabilized zirconia (PSZ, 3% yttria), which is 80% tetragonal and 20% cubic.

Many approaches (e.g., co-fired monolithic structures) are still experimental or even conceptual as methods of constructing large stacks. Unlike the 0.6–1.0 m² cells proposed for the MCFC, planar ceramic SOFC components are restricted to perhaps 100 cm² or a little larger. For these systems, bipolar structures (e.g., ribbed lanthanum chromite or lanthanum iron cobalt chromite doped with Mg²⁺ or preferably Sr²⁺ or Ca²⁺) or, more recently, stable alloys with correct expansion characteristics (oxide-coated if required at the cathode side) are being developed. The most mature cells are tubular systems designed by Westinghouse, see ref. 27, which now uses the electronically conducting air electrode itself as a support tube, and are capable of 0.7 V at 200 mA cm⁻² or 0.67 V at 300 mA cm⁻² on reformat at 85% utilization. Tubes 1 m in length and about 1.6 cm diameter have an active area of almost 450 cm².

Conclusions

Today's fuel cells may be classified in various ways, i.e., by their temperature of operation (high-, medium-, and low-temperature fuel cells) or by the type of electrolyte they use. The latter classification is perhaps the most convenient and logical, since it determines the operating temperature range, the operating characteristics, the materials which can be used, the type of catalysts required, and the overall performance.

Alkaline fuel cells (AFCs) are confined to using KOH, since potassium carbonate is more soluble than the sodium salt. Hydrogen which is as CO₂ free as possible is the required fuel. In alkaline electrolytes, hydrogen reacts producing electrons and water at the anode. Hence, if pure hydrogen is used as fuel, it is diluted by water vapor as it passes through the anode chamber. It is not possible to consume all of the hydrogen, since if this were to be so, both the current density and the reversible hydrogen potential versus that of the oxygen electrode (i.e., the cell potential), would go to zero. In consequence, the hydrogen is generally operated in a feedback loop in which a condenser continuously removes water vapor, discharging the latent heat of evaporation. In such cases, the hydrogen fuel may be operated at 30% utilization per pass, depending on the temperature. Aerospace AFCs, such as the United Technologies 12 kW PC-17C units in the Space Shuttle Orbiter, operate on this principle using pure oxygen as oxidant, at 4 atm pressure to increase performance and thus render the system more compact. A review of alkaline technology is available [23].

For terrestrial applications, pure hydrogen is generally not available for common fuel cells, which nevertheless operate on hydrogen. Fuel cells must be supplied with fuel manufactured from hydrocarbons, e.g., natural gas by steam reforming and water-gas shifting, if required. The fuel consists of various mixtures of H₂ and CO and/or CO₂. Just as it is not feasible to separate pure oxygen from air, extraction of pure hydrogen from such mixtures is considered to be neither energetically nor financially economical. In spite of the potential advantages of the AFC, i.e., the lower absolute cathode potential compared with acid electrolytes, which greatly increases the range of catalytic and constructional material which can be used, the lack of availability of hydrogen has severely limited the terrestrial use of the AFC. Its cathode shows higher performance

than that of acid fuel cells, even using non-noble catalysts (ref. 2, p. 406). If inexpensive materials, including carbon and plastics, are to be used in AFCs, the operating temperature should be limited to about 353 K.

Provided that it operates at temperatures over 423 K, the PAFC could supply free waste heat for reforming natural gas. At a steam-to-carbon ratio of 3, this represents 16.3% of the LHV of natural gas fuel, considerably improving overall system efficiency. At about 463 K, it shows good tolerance to poisoning by CO in amounts less than about 1–1.5% by volume. The original challenge presented by the PAFC was that of the high cost of materials. According to Pourbaix [28], only niobium, tantalum, gold and platinum and certain of its relatives are thermodynamically stable under PAFC cathode operating conditions, even at ordinary temperatures. Platinum (or its alloys) was the only stable active cathode catalyst available. By the early 1970s, it had been shown that various carbons were kinetically, if not thermodynamically, stable at the cathode, and could show reasonable lifetimes. After graphitization, stabilities were even better. Careful work showed that corrosion was dependent on the partial pressure of water vapor and temperature, which allowed definitions of the temperature and pressure ranges in which stable operation could be expected. This led to the development of low-loading platinum electrodes supported on carbon and graphite structural elements, which could be fabricated at low cost in mass production [29]. Performance limits the PAFC to operation above 423 K, and materials considerations put the upper limit at 473–478 K (under pressure). Its performance on natural gas reformat has increased to as much as 325 mA cm^{-2} at 0.62 V at atmospheric pressure.

Phosphoric acid is not an aqueous acid under PAFC operating conditions, but a molten self-ionizing acid. In contrast, aqueous acids cannot be used at temperatures exceeding about 90 °C, since they then cease to conduct protons as water is lost. The only aqueous acid fuel cell used today is the PEM system, which uses perfluorinated organic polymer sulfonic acid as the electrolyte. Unlike the PAFC, it is not CO tolerant, and it cannot supply steam using waste heat. On pure hydrogen, its performance is now excellent between ambient temperature to its maximum operating temperature, even with very low-loading carbon-supported platinum cathodes (for which no substitute has been yet found). New polymeric materials, including fluorinated disulfone imide acid, may be attractive, but they will not extend its operating temperature range. The PEM system presently suffers from the cost of the polymer membrane, which costs US\$ 600–2000 per m^2 (US\$ 4.50–18 per g), i.e., US\$ 290–950 per kW at today's atmospheric pressure performance at low platinum loading. This is in contrast to US\$ 9 per kW for the platinum catalyst materials cost at a loading of 0.1 mg cm^{-2} (cathode) and 0.05 mg cm^{-2} (anode). It is hoped that these PEM costs will fall from pharmaceutical levels to about US\$ 200 per kg (US\$ 20 per kW for thin membranes) as production increases. Meanwhile, the use of sandwich membranes may be possible (as in the SOFC), in which fully fluorinated material is only incorporated in the cell where it is required. Interesting possibilities are represented by polyphosphazine or other unusual backbones with wholly or partially-fluorinated acidic side-chains. It seems unlikely that truly stable alkaline polymer electrolytes using quaternary ammonium groups can be made, since fluorination makes these materials weak bases.

The reversible thermodynamics of the SOFC seem to put it at a disadvantage compared with the MCFC, as do its relatively small cells. However, it is less polarized than the MCFC due to its higher operating temperature. While materials costs may eventually fall to low levels, at present, it must operate at high current densities to be economical. In practice, it is less limited by utilization considerations than simple MCFC systems. It may operate at 85% or even 90% utilization.

Perhaps more important is the fact that both O_2 and CO_2 in the MCFC are reactants in the cathode process. In effect, they compete for space. A practical MCFC system with a competitive capital cost operating at 1 atm pressure may require the addition all of the anode effluent (including product water and any water vapor remaining from reforming) into the cathode air stream. In an MCFC operating with 67% cathode recycle and 50% CO_2 utilization per pass, the mean cathode gas composition in the cell will only be 7% O_2 /7.5% CO_2 at an overall O_2 utilization of 30%. As a result, the effect of the two reactants on the reversible thermodynamic Nernst equation is certainly increased compared with a case where no CO_2 is needed, i.e., in the SOFC. The MCFC case, the mean cathode gas composition gives a 156 mV reversible Nernst voltage loss at 923 K, due to the effect of the $(RT/4F) \log(pO_2)(CO_2)^2$ term. In contrast, the theoretical reversible loss in the SOFC is only 47 mV at 1273 K at a mean oxygen utilization of 10% (18% O_2 mean). This makes up for the difference between the standard state reversible potentials (1013 mV at 923 K and 909 mV at 1273 K).

This thermodynamic disadvantage of the MCFC is compounded by a kinetic disadvantage, since reaction rates are reduced at low reactant partial pressure, hence overpotentials are increased. As a result, kinetics and thermodynamic considerations in an MTFC operating at 923 K or in an SOFC operating at 1273 K tend to compensate each other. Thus, optimized MCFC and SOFC fuel cells may have about the same overall electrical efficiency. In both cases, their high quality waste heat will serve for sensible heat reforming, for cogeneration, and for bottoming cycles in large systems.

Performance puts a lower limit on the MCFC's operating temperature equal to about 890 K, and materials considerations put an upper operating limit on the MCFC of about 950 K. A major issue is the reduction of the polarization slope in the MCFC to about half of its present value of $1.1\text{--}1.2 \Omega \text{ cm}^{-2}$ to allow an increase in power density. A further major aim is to reduce the practical working temperature of the SOFC from today's 1223–1273 K to the 1073 K range. This may be carried out using ultra-thin YSZ cell structures and metal bipolar plates or completely new electrolyte materials, if necessary of sandwich type, if incompatibilities under anodic or cathodic conditions occur. These may require new families of anode cermets, and cathode materials. They are reviewed by Steele [30]. The main impetus for low temperature operation is the elimination of very costly superalloy or ceramic heat exchangers for air preheating, and their replacement with stainless steel. This change may come about with no loss in performance, slower kinetics being compensated by reversible thermodynamics. We should note that the Westinghouse tubular system contains a built-in ceramic preheater, in which air enters at 600 °C.

The temperature windows for different electrolytes are limited by performance at the low end and materials considerations at the high end. As a result, there are no electrolytes capable of operation between 360 and 420 K, between 480 and 890 K, and between 950 and 1220 K. Development of electrolytes for these temperature ranges would be valuable to reduce materials requirements for the SOFC for operation between 950 and 1220 K, and for the development of direct methanol (or internal reforming) systems operating in the 480–890 K range.

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