

THE USE OF CENTRIFUGAL FIELDS IN ELECTROCHEMICAL ENERGY CONVERSION

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The conversion and storage of energy by means of electrochemical processes can be greatly enhanced by the utilization of centrifugal fields. Such system-wide fields pervade both the macro-scale, at which hydrodynamic flow processes occur, and the micro-scale at the electrode surface where electrochemical reactions proceed. This paper describes how intense centrifugal acceleration might be exploited to increase the electrochemical reaction rates in fuel cells and batteries, and thus to improve their overall performance characteristics. Some recent findings in the development and testing of a novel prototype centrifugal fuel cell are presented to indicate possible trends and future prospects of this approach.

ABSTRACT

The earliest designs of fuel cell date back to William Grove's pioneering experiments ¹ of 1839, an indication that fuel cells are by no means a recent invention. The development of 'modern' fuel cells over the last half century – since the introduction of Bacon's 6kW fuel cell ²⁻³ in the late 1950's – has however been particularly fervent as the search for clean efficient power sources has intensified. Whilst many different types of fuel cells ⁴⁻⁵ and batteries ⁶⁻⁷ have been successfully developed – all based largely on a static configuration of electrodes – the underlying electrochemical processes involved have changed very little. Indeed, progress in materials science has perhaps contributed more to the increased efficiencies of today's electrochemical energy conversion devices than has any radical changes in the basic reaction processes involved. Apart from a few designs for specialized military applications, the geometrical arrangements used in today's fuel cells and batteries are essentially the same as those of 160 years ago, i.e. multiple pairs of electrodes fixed in a stationary housing containing an electrolyte. Current improvements are certainly due to the selective use of new electrode materials (especially catalysts), significantly higher operating pressures and temperatures, and the improved compositions of the reactants and electrolytes, all of which have led to worthwhile increases in performance. It is remarkable therefore that the advanced electrochemical systems now being developed, whether for the direct generation of electricity or the production of industrial gases and chemicals, should still suffer the same basic hydrodynamic limitations as in Bacon's, and indeed Grove's, earliest devices. These limitations restrict the power output of all electrochemical energy conversion devices and originate in the inherent slowness of the diffusion processes that occur near the electrode surface. To increase the power output – and to make better use of new porous media electrodes now being developed – the design of future electrochemical systems must shift away from diffusion-limited reaction processes to forced-convection hydrodynamic mass-transfer at the electrode surfaces.

The merger of electrochemistry with hydrodynamics brings together micro-scale phenomena, at the electrochemically active sites within the pores of the electrode, with macro-scale multiphase flow processes taking place at the system level. Such a merger of phenomena occurs with the application of centrifugal fields and an understanding at both macro- and micro-scales is necessary if progress in the utilization of real 3-dimensional porous electrodes is to be achieved.

Many types of fuel cell and battery use air or oxygen in combination with gaseous, liquid or solid fuels. In most, if not all, metal-air battery/fuel cell systems, for example, the 'rate-determining-step' in the energy conversion process occurs at the oxygen electrode. Charge transfer at the electrolyte-electrode surface is governed almost entirely by the transport of ions in solution across a liquid film from the gas-electrolyte interface. Even with electrolyte solutions saturated with the reactant gas, mass transfer at the reaction site depends on the slow molecular diffusion of the ionic species across a liquid film, and this limits the maximum achievable current. The parameters influencing this limiting current density are the local concentration gradients, diffusion coefficients, the diffusion boundary layer thickness, the active area available for reactions, and, most importantly, the hydrodynamic flow conditions.

With conventional 'stationary' electrodes, static diffusion controls the mass transfer rate even if the electrolyte and the reactants are pumped around the cell. In pumped forced-flow systems, the reactant fluids are of necessity supplied under pressure to the electrode surface, although no forced convection *through* the electrode occurs. Diffusion, ultimately, is the only means for transferring charge across the wetted film separating the injected reactant gas from the electrode, and the diffusion rate depends critically on the prevailing concentration gradient. As a result, today's fuel cell industry has grown up ostensibly around porous flat-plate or tube-type electrodes. Porous gas-diffusion electrodes have a dry hydrophobic 'gas-side' and a wet hydrophilic 'electrolyte-side', separated by a thin wet-proof layer. This layer (usually a PTFE binder) permits gas flow from one side, but is impermeable to the flow of liquid electrolyte from the other. Conventional two-layer electrodes have one region with relatively coarse pores on the gas-side through which reactant gas is admitted, and a second layer of fine pores which remain filled with liquid electrolyte. Electric current is generated at the 3-phase boundary where these layers come together. Even as far back as Grove, the 'rule' has always been that *the electrodes must not be completely flooded*. Because the flooded parts of an electrode contribute little to the production of electric current, the electrodes must therefore be made as thin and as close-fitting as possible. Planar porous electrodes are therefore essentially two-dimensional structures although much effort has gone into increasing the electrode material's specific surface area at the molecular level to increase power production in the electrochemically active reaction zone.

A three-dimensional porous electrode should ideally permit the flow of reactants *through* its interior, not just across its outer surface. Such an 'open-flow' topology facilitates generating current more homogeneously throughout the entire volume of the electrode, and should eventually permit very large current densities to be achieved. In practice, actual power densities are limited by ohmic losses in the solid and liquid-filled regions of the electrode, and by over-potential voltage drops across the 'electric double-layer' at the electrode surface. It might appear that in such a configuration the 'rule' regarding the non-operability of flooded electrodes would be violated. However, this no-flooding rule applies only to the 'conventional' two-sided gas-diffusion electrode because of its geometry, not through any fundamental law of electrochemistry. The normal 'partially-flooded' operating state of a gas-diffusion electrode should be seen therefore as a stationary state of an otherwise highly transient process. Thus, when gas is transported through the capillaries of a 3-dimensional porous electrode in the presence of a co-flowing electrolyte, the electrochemical reaction will occur through a *forced-convection two-phase flow* of reactants. The Nernst diffusion limit is then no longer applicable and the reaction is driven by the hydrodynamics of the flow process itself. Moreover, the three-phase boundary at the gas-electrolyte-solid interface is no longer constrained to a planar reaction zone at the surface but spatially penetrates the entire volume of the electrode. This extended three-phase reaction boundary is thereby dynamically distributed throughout the electrode, constantly creating and destroying the wetted films around the sites where current is generated, thus increasing the overall power density.

To date, little progress has been made in designing fuel cells to work with extended 3-dimensional

porous electrodes. This paper outlines an approach⁸ based on the development of a novel type of electrochemical energy-conversion device – the *Centrifugal Fuel Cell*. This device is designed to exploit intense centrifugal fields to establish a hydrodynamic flow of electrolyte around the cell and through the electrodes to improve the charge-transfer process. In particular, the paper describes how *spin-enhanced natural convection* can induce forced-convection mass transfer at the electrode surface, without the need for mechanical pumps. Recent experience in the development and testing of a rotating zinc-air cell will be discussed and some scaling considerations will be presented to emphasize how centrifugal acceleration can be used to optimize the increased power output of such systems.

Some of the models commonly used to describe the kinetics of electrode reactions in porous media will be reviewed in the context of applied centrifugal fields. In relation to spin-enhanced natural convection, the physicochemical hydrodynamics methods⁹⁻¹⁰ relevant to high Reynolds number turbulent flow are then found to be more appropriate than Nernst-type laminar diffusion models used for describing 'static' electrochemical systems. It can be expected that forced-convection, with no external pumping, can be promoted in a centrifuge system with only a modest input of energy to maintain rotation. The benefits are manifest in attaining a higher reaction rate resulting from the reduction in boundary layer thickness, leading to an increase in limiting current density. Compared to systems with stationary electrodes operating under normal Earth gravity ($g_0 = 9.81 \text{ m/s}^2$), the buoyancy forces on the (bubbly flow) gas phase in a centrifugal system are greatly increased and permit a potentially much higher throughput of gaseous fuel or oxidant. These increases are empirically related to the angular spin speed ω and the 'centrifugal acceleration enhancement factor', $E_c = \omega^2 r / g_0$. For compact systems, the radial inflow over the electrode is strongly convergent and leads to further acceleration and thinning of the boundary layer, giving a higher 'disk-averaged' mass transfer rate. Other factors, such as the increased bubble rise velocity and the higher partial pressure of the supplied reactants, lead to additional improvements in the overall performance and these macro-scale hydrodynamic effects play an important role at the microscopic level of the catalytic regions within the porous electrode.

In summary, an alternative approach to the conceptual design of future electrochemical energy-conversion systems will be presented to indicate where centrifugal fields might be exploited to develop more efficient and compact fuel cells in which high-active 3-dimensional porous electrodes can be used to maximum advantage.

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