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Higher Power Output in a PEMFC Operating under Autonomous Oscillatory Conditions in the Presence of CO

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Time-averaged cell voltage, cell efficiency, and power density in an autonomous oscillatory state was higher than that in stable steady-state for a proton exchange membrane fuel cell (PEMFC) operating in the presence of CO in the anode feed reformate gas. The average power density under such an oscillatory state at 55°C is twice that under a stable steady state. The average cell voltage and power density gain are due to the decrease of the time-averaged anode overpotential in the oscillatory state. This report thus provides experimental evidence that autonomous oscillatory operation of fuel cells in the presence of CO can increase the power output as compared to that in stable steady-state operation.

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Periodic or chaotic behavior has been observed in both homogeneous and heterogeneous reaction processes, and especially in electrochemical systems. If such systems are well-mixed, only temporal periodic variations of the variables appear. Otherwise, spatiotemporal patterns may be observed, e.g., in the concentration of adsorbed species on an electrode surface. The literature is replete with reports of oscillatory phenomena in electrochemical systems, and the mechanistic understanding of the origin of such oscillations is being continually advanced. Generally, the periodic behavior of an electrochemical system is due to the interplay of nonlinear electrode kinetics, mass transport, and the external electrical circuitry. The mathematical models for these phenomena contain nonlinear differential equations for reactant concentrations, coverage of surface species, and current or voltage as variables.

Oscillations in reaction systems were considered puzzling and largely irrelevant. Later, there was an effort to search for ways to exploit nonlinear kinetics. For instance, the reaction rate is increased in a forced oscillatory biochemical reaction. Similar phenomena were also observed in conventional chemical reactions with nonlinear kinetics. In these examples it was demonstrated that efficiency could be improved by operating in a forced oscillatory state. With the improved theoretical understanding of periodic behavior in electrochemical systems, the expectations of their practical utility are also increasing.

Recently, we found that sustained potential oscillations exist in proton exchange membrane fuel cells (PEMFCs) fed with H2 containing low levels of CO when operated under constant current conditions. The oscillations were determined to be due to the nonlinear kinetics of the anode reactions coupled with the mass and charge conservation. Here we present our findings on increased power output of PEMFCs when operated under such oscillatory conditions.

Experimental

The experimental details can be found in our previous work. In short, two pieces of electrode were bonded to either side of a solid polymer electrolyte membrane (Nafion 115). An electrode containing 0.35 mg/cm2 PtRu (atomic ratio 1:1, E-TEK) was used at the anode, exposed to a simulated reformate gas (H2 containing low levels of CO, also containing 20% CO2 in some experiments). The cathode containing 0.4 mg/cm2 Pt (E-TEK) was exposed to humidified O2. A membrane electrode assembly (MEA) with 5 cm2 effective electrode area was prepared by hot-pressing at 130°C and under a pressure of 4000 lb for about 2 min. The MEA was tested in a single cell (Electrochem, Inc.) in a test station with temperature, pressure, and mass flow control. The total pressure at both anode and cathode chamber was 30 psig. The volumetric flow rates reported in this study are all in units of standard (1 atm and 25°C) cubic centimeters per min (scm). An electronic load (HP 6060B) interfaced with a PC was used to measure the current-voltage characteristics of the fuel cell.

Results

The performance of a fuel cell in the laboratory may be experimentally evaluated under constant voltage, constant current, or constant resistance modes with an electronic load. We observed sustained potential oscillations when a fuel cell fed with H2/CO was operated under the constant current mode, with the anode catalyst being PtRu. Since oscillations were not observed when the fuel cell was operated under the constant voltage or constant resistance mode, it is possible to directly compare the performance under an oscillatory state with that in a stable steady state.

The fuel cell current-voltage relationship at room temperature obtained for a H2 feed containing 100 ppm CO under constant voltage mode (stable steady-state) is shown in Fig. 1 along with the corresponding power output (in units of mW/cm2). Even though the open-circuit voltage is around 1.0 V, the cell voltage drops precipitously to 0.4 V, even when only a small current (i.e., 30 mA/cm2) is drawn. Such a large initial drop in cell voltage is due to severe poisoning of the PtRu catalyst by CO at room temperature. The peak power output was only around 40 mW/cm2, which occurs at a current density of about 200 mA/cm2.

The time-averaged cell voltage and power density corresponding to Fig. 2 are plotted in Fig. 3. The time-averaged cell voltage does not change greatly as a function of current density. The time-averaged power output thus increases almost linearly with the current density in the range investigated. Further, the time-averaged cell voltage is substantially higher when compared to the stable steady-state value (Fig. 1). For example, at a current density of 200 mA/cm2, if the fuel cell were operated at a stable steady state, i.e., in the constant voltage mode, the cell voltage is only about 0.2 V, while under the oscillatory state, the time-averaged cell voltage is almost 0.5 V. Thus, it is evident from a comparison of Fig. 3 and 1 that the time-averaged power output when operated under oscillating conditions is twice that under a stable steady state.

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tory conditions is substantially higher than that under stable conditions. Similar results were obtained for a H₂ feed containing 100 ppm CO and 20% CO₂, as well as for a H₂ feed containing 200 ppm CO.

The performance of the fuel cell operated with a H₂/108 ppm CO anode feed under stable steady-state conditions is summarized in Fig. 4. The fuel cell performance is poor at low temperatures. Further, no limitation imposed by transport of reactant gases is evident from the polarization curves in the current density range investigated. The corresponding power density is plotted in Fig. 5. The power output improves with the increase of fuel cell temperature, which is attributable to both reduced CO affinity for the catalyst surface, as well as enhanced H₂ and CO electro-oxidation rates. The peak power output thus, at 55°C is about 90 mW/cm², while the peak power density at 80°C is about 180 mW/cm².

Figure 6 shows the time-averaged cell voltage and power density under the autonomous oscillatory state at a fuel cell temperature of 55°C. The average cell voltage decreases gradually with the current density, and is higher than that in Fig. 4 for the same current density. The time-averaged power density in the oscillatory state shown in Fig. 6 is nearly double when compared to that in Fig. 5 at 55°C (i.e., 150-200 mW/cm² vs. about 90 mW/cm² maximum). This power output is even higher than the maximum at 80°C for the stable steady state. Moreover, the power output at 55°C in the oscillatory state shown in Fig. 6 may not have peaked yet.

Discussion

Autonomous oscillations were observed at temperatures below about 70°C. A quantitative mechanistic model and analysis has been given by us before. Qualitatively, when CO builds up on the catalyst surface, i.e., as θCO increases, the anode becomes increasingly polarized to a higher potential to compensate for a smaller θH and to sustain the applied constant current. The anode overpotential increase accelerates the electro-oxidation of CO_ad on
the catalyst surface via oxygen-containing surface species such as OH
ad, which is formed more readily on the catalyst surface at
the catalyst surface via oxygen-containing surface species such as
OHad, which is formed more readily on the catalyst surface at
current density. Thus, the catalyst surface via oxygen-containing
surface species such as OHad, which is formed more readily on the
catalyst surface at low overpotentials and can be electro-oxidized
at high overpotentials could conceivably cause oscillatory behavior.

Self-organized potential oscillations occur at conditions far from
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thermodynamic equilibrium with the presence of appropriate feed-
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feedback loops. As discussed above, the dynamic instability is linked to
feedback loops. As discussed above, the dynamic instability is linked to
the interplay of the electrode kinetics and the external electrical
circuit trying to sustain a constant current. A negative differential
resistance ($\delta V/\delta i < 0$), i.e., when the total current decreases with
an increase of electrode potential, is necessary for the existence of
electrochemical instability, which has been shown to exist in the
anode potential oscillations in this study. The following processes
have been identified as essential for the occurrence of these
oscillations: (i) a current carrying process (H electro-oxidation,
which depends upon the anode overpotential); (ii) a process respon-
sible for the occurrence of the negative differential resistance
(potential-dependent adsorption and desorption of OH); and (iii) a
potential-dependent process in which potential has a positive effect
on the reaction rate (reactive removal of CO). The temporal evolu-
tion of the anode reaction system is explained quantitatively by the
differential equations derived from charge as well as mass balance.
By applying the linear stability analysis, i.e., by the sign of the
eigenvalues of the associated Jacobian matrix of the linearized equa-
tions governing the system, a Hopf bifurcation has been shown to
exist in this system.

The oscillatory fuel cell voltage reflects the sustained effort for
self-recovery on part of the catalyst surface to maintain a given
current. The increased power output in the oscillatory state is evi-
dently caused by the time-averaged cell voltage increase at a given
current density. The increased average cell voltage is a result of the
decreased average anode overpotential. It has been shown computa-
tionally and experimentally that under oscillatory state, the rise
and fall of overpotential in a cycle is not symmetrical about the unstable
steady-state value. The deviation of the minimum overpotential is
larger than that of the maximum overpotential. Furthermore, for a
large fraction of the time in a cycle, the anode overpotential is at a
lower value than that under a stable steady state. Such a gain in the
decrease in anode overpotential for a substantial fraction of the time
in a cycle leads to the higher average cell voltage in the oscillatory
state. The increased power output in the oscillatory state is consist-
tent with the oscillations appearing due to the effort by the system
to maximize the entropy production rate $\sigma_s$. In the fuel cell system,
this is equal to current (reaction rate) times cell potential (which is
proportional to the affinity of the reaction system). The relation is
shown by the following equation

$$\sigma_s = \frac{1}{T} \frac{\partial r}{\partial T} = \frac{zF}{T} V_i$$

where $\sigma_s$ is the entropy production rate, $T$ is temperature, $A$ is
the affinity, $r$ is the reaction rate, $z$ is the number of electrons in the
reaction, $F$ is the Faraday constant, $V$ is cell voltage, and $i$ is the
current. Thus, the rate of entropy production in a fuel cell is nothing
but the rate of power production. We have shown that the phase
angles of variables such as the surface coverage of CO, H, and OH
are different. Phase lag among variables leads to different phase
angles between the reaction rate (current) and affinity (voltage)
of the system. This phase relation between affinity and reaction rate
is another factor in determining the power output of a system.

There has been an attempt to accelerate reaction rate or decrease
the oxidation potential for the electro-oxidation of formic acid by
forced oscillation, i.e., by superimposing a periodic potential or
current signal with a certain amplitude and frequency on the stable
potential or voltage. In a certain range of frequency used, either the
oxidation current is increased or the overpotential is decreased, im-
plying an advantage of forced oscillatory operation over stable
steady-state operation. The gain in both reaction rate and effi-
ciency has been demonstrated in biological reactions as well, where
the biochemical reaction system exhibits autonomous oscillations.
A perturbation to one of the reactants (i.e., oxygen influx) in the
form of a sinusoidal wave was used instead of steady flux. It was
found that several of the thermodynamic quantities were changed as
compared to the undisturbed state. The phenomenon is believed to
be due to resonance, which is a generic feature of oscillatory sys-
tems. Reaction rate enhancement in other chemical reaction systems
has also been observed via forced concentration oscillations of
reactants. There is a significant improvement of the time-averaged

Figure 5. Power output of stable steady-states (constant voltage mode) for
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various cell temperatures shown in Fig. 4.

Figure 6. Time-averaged cell voltage and power output at different current
densities in autonomous oscillatory state (constant current mode). $T_{cell} = 55^\circ C$; anode feed: $H_2/108$ ppm CO; anode inlet flow rate: 48.1 sccm.
production kinetics, while for linear kinetics there is no improvement.\(^{17}\)

While advantages are reported for these forced oscillatory reactions, almost all the examples demonstrated so far need an external oscillatory signal to force the reaction system into an oscillatory state. However, results reported here provide evidence that a system operating under an autonomous oscillatory condition also shows power output gains as compared to that at a stable steady state under otherwise identical experimental conditions. Although the periodic forcing of the external parameters (e.g., reactant flow rates, current, or cell voltage) may not be difficult in an energy conversion device such as a fuel cell, cumbersome external control for periodic forcing is generally undesirable. Thus, our observation may be useful in managing power output for fuel cells, where the control of cell or stack current is not difficult. Although the periodic nature of voltage output would generally be undesirable, it is not a significant problem to condition this with modern electronic circuitry. Furthermore, the overall stack voltage may actually be less periodic, perhaps approaching the total average value due to the phase angle difference in cell voltage of the single oscillator (single cell) within a stack.

Undoubtedly, raising the cell temperature can increase the power output of a fuel cell operating under a stable steady state. However, the PEMFC operating temperature usually cannot exceed about 80-90°C due to limitations imposed by the current polymer electrolyte membrane. Thus, utilizing the oscillatory kinetics may serve as an alternative approach to improving the power output (and thus managing CO poisoning) of a reformate-fed fuel cell. However, even in the oscillatory state operation, the power output is not comparable to that with pure hydrogen. Nevertheless, the present results provide evidence that operation under autonomous oscillatory conditions (due to the inherent nonlinear kinetics in electrode reactions) can increase the power output as compared to that under a stable steady-state operation in an energy conversion device. This has been expected and hoped for by researchers working on nonlinear dynamics in electrochemical systems.\(^{3}\)

Conclusions

A PEMFC can be operated in an autonomous oscillatory state under constant current conditions when reformate is used as the anode feed. Compared to the stable steady-state operation, the time-averaged cell voltage, efficiencies, and power density are higher under the oscillatory state. The increase in average cell voltage and power density is due to the decrease of the time-averaged anode overpotential under oscillatory conditions. There are relatively sharp bursts in the anode overpotential only periodically to rid the surface of the poisoning species. These observations may be useful for developing an operational strategy for improved management of power output in PEMFC’s in the presence of CO.

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