Short communication

Efficiency of electrochemical systems

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Abstract

The second-law efficiency is proposed for measuring and comparing the performance of electrochemical processes. It measures how close the process approaches a reversible process. Other definitions of efficiency found in the literature based on the first law of thermodynamics can generate efficiency values that are >100% for certain systems depending on whether the change in entropy for the overall chemical reaction involved in the process is positive or negative. Such efficiency values are misleading while making it difficult to compare processes that absorb or release significant quantities of thermal energy. Use of the proposed efficiency which is within the frame work of the second law of thermodynamics, can reach 100% only in the limit of a reversible process and will always stay <100% whether the entropy change is positive or negative. Furthermore, it accounts for the quality of thermal energy added to or removed from the system and thus provides a more consistent way of comparing different types of electrochemical devices. This consistency will allow better comparison of performance on a widespread basis, i.e., between groups working on distinct electrochemical systems.
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1. Introduction

The performance of an electrochemical device such as a fuel cell when measured in terms of the thermal efficiency or the "first-law efficiency" of the system can be quite misleading. Expressing the performance in terms of the thermal efficiency does not provide a true yardstick to measure the inefficiencies within the system since not all of the energy released by reaction within the cell may be converted to useful work without violating the second law of thermodynamics. Furthermore, as pointed out by [1], the thermal efficiency of a fuel cell can be >100% in cases where the entropy change for the overall reaction occurring within the cell is positive. This can be seen from the following.

The expression for the thermal efficiency (η_{FC}) of a fuel cell is defined by the expression:

$$\eta_{FC} = \frac{W_{out}}{-\Delta H_R} \tag{1}$$

where W_{out} is the useful work produced by the process, and ΔH_R is the enthalpy change for the reaction.

From the first law of thermodynamics:

$$\eta_{FC} = -\frac{\Delta H_R - Q_{in}}{-\Delta H_R} \tag{2}$$

where Q_{in} is the heat added to the system. For a reversible fuel cell operating isothermally at a temperature T, the thermal efficiency then becomes

$$\eta_{FC} = \frac{-\Delta H_R + T\Delta S_R}{-\Delta H_R} \tag{3}$$

$$= \frac{-\Delta G_R}{-\Delta H_R} \tag{4}$$

where ΔS_R is the entropy change and ΔG_R is the Gibbs free energy change (represents the maximum useful work that may be produced) for the reaction. As can be seen from Eq. (3) above, for a reaction that releases energy where ΔH_R is negative, efficiencies >100% can be calculated when ΔS_R is positive.

To circumvent this problem of calculating efficiencies >100% while comparing the thermodynamic performance of fuel cells with heat engines, two separate definitions for the thermal efficiency of a fuel cell depending on whether ΔS_R is positive or negative have been suggested [2]. In cases where ΔS_R is negative, the above expression is utilized while when ΔS_R is positive, η_{FC} is always reduced to 100% by replacing the denominator in the above expression

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with $-\Delta H_R + T\Delta S_R$ or $-\Delta G_R$. This methodology, however, leads to an inconsistent set of yardsticks when comparing the performance of different types of fuels in a fuel cell.

Next, in the case of an electrolyzer, an energy efficiency (η_{EL}) has been defined [3] by the ratio of the thermoneutral cell voltage ($U_{TN} = \Delta H_R' / zF$) and the actual cell voltage (U_{ACT}):

$$\eta_{EL} = \frac{U_{TN}}{U_{ACT}} \tag{5}$$

$$= \frac{\Delta H_R'}{zFU_{ACT}} \tag{6}$$

where z is the number of electrons transferred per reaction, and F is the Faraday constant. The above expression may also be written as

$$\eta_{EL} = \frac{\Delta H_R'}{\Delta G_R' + zFU_{OV}} \tag{7}$$

$$= \frac{\Delta H_R'}{\Delta H_R' - T\Delta S_R' + zFU_{OV}} \tag{8}$$

where U_{OV} is the cell overvoltage, and $\Delta H_R'$, $\Delta G_R'$ and $\Delta S_R'$ are the changes in enthalpy, Gibbs free energy and entropy for the decomposition reaction, i.e., the reaction proceeding in the opposite direction of that in a fuel cell when, e.g., a water electrolyzer and a H_2 based fuel cell are being considered. Efficiencies >100% can also be calculated using this definition for systems when $T\Delta S_R' > zFU_{OV}$.

2. The second-law efficiency

In order to overcome the limitations discussed in the preceding, it is proposed that the "second-law efficiency" [4] be utilized for measuring or comparing the performance of such electrochemical devices or processes; the general form defined as

$$\eta_{II} = \frac{\sum \chi_{out} + Q_{out}(1 - T_0/T_{out}) + W_{out}}{\sum \chi_{in} + Q_{in}(1 - T_0/T_{in}) + W_{in}} \tag{9}$$

where η_{II} is the second-law efficiency, $\sum \chi_{out}$ and $\sum \chi_{in}$ are the sum of the exergies of the streams leaving and entering the system, respectively, T_{in} is the temperature at which heat (Q_{in}) is added to the system, T_{out} is the temperature at which heat (Q_{out}) is removed from the system, T_0 is the temperature of the surroundings (in practical applications, would be the mean temperature at which heat may be rejected to the surroundings such as cooling water). The second terms in the numerator and the denominator of Eq. (9) express the Carnot cycle efficiency of converting the heat to work. W_{out} and W_{in} are the useful work developed by the system and that expended on the system, respectively (e.g., electrical in the case of an electrochemical process) while exergy of a stream is the maximum work producing capability of the stream as it is equilibrated with the surroundings.

The above expression for the second-law efficiency measures how close the process approaches a reversible process. This efficiency definition which is within the frame work of the second-law can reach 100% only in the limit of a reversible process and will always stay <100% whether the entropy change for the reaction is positive or negative. It also provides a true measure of how much of a gain in performance can be realized by making improvements to the process or device. Furthermore, it accounts for the quality of thermal energy added to or removed from the system and thus provides a more consistent way of comparing different types of electrochemical devices. The second-law efficiency comparison also provides a standard methodology, which if universally adopted may provide a consistency that may be presently lacking in the fuel cell/electrolyzer community. This consistency could allow better comparison of performance on a widespread basis, i.e., between groups working on distinct electrochemical systems.

3. Exergy

Use of exergy to study system performance has been reported in literature by many investigators (e.g., [5–7]). When the kinetic and potential energy effects may be neglected, exergy (χ) for a stream is defined as [5]:

$$\chi = W_{sensible} + W_{expansion} + W_{concentration} + W_{chemical} \tag{10}$$

where $W_{sensible}$ is the reversible work that may be obtained by a heat engine taking heat from the stream (at temperature T) and rejecting heat to the environment (at temperature T_0), $W_{expansion}$ is the reversible work that may be obtained from the stream at pressure P by isothermal expansion (after conversion of the sensible heat) to the pressure of the environment (P_0), $W_{concentration}$ is the additional work that may be obtained by reversibly diffusing a noncombustible component i within the stream at partial pressure P_i through a membrane to the environment where it may be at a partial pressure of P_{0i}, and $W_{chemical}$ is the work (after cooling and expansion) that may be produced by oxidation of the combustibles that may be present in the stream with enough excess air such that the partial pressure of the CO_2 corresponds to that in the ambient. Thus,

$$\chi = -\int \left(1 - \frac{T_0}{T}\right) C_p \, dT$$
$$+ RT \left[\ln\left(\frac{P}{P_0}\right) + \sum \ln\left(\frac{P_{i0}}{P_i}\right)\right] - \Delta G_{reax} \tag{11}$$

where the integral in the first term on the left-hand side of Eq. (11) is evaluated from the initial to the final temperature of the stream, C_p is the specific heat of the stream, ΔG_{reax} is the Gibbs free energy change for the oxidation reaction of the combustibles at the temperature of the environment.

The first term on the left-hand side of Eq. (11) defines the maximum work that may be obtained based on the Carnot

cycle efficiency. This term as defined in [5] is modified to include the work potential of streams that contain water in the form of vapor which could undergo a phase change when equilibrated with the environment. This term (W_{heat}) is defined as

$$W_{\text{heat}} = -\int \left(1 - \frac{T_0}{T}\right) dH \tag{12}$$

where H is the enthalpy which may include both sensible as well as latent heats.

The second term of Eq. (11) is modified in order to be able to handle streams that contain water as a vapor or as a liquid and may undergo phase change:

$$W_{\text{expansion}} = -\Delta G_{\text{expansion}} \tag{13}$$

where $\Delta G_{\text{expansion}}$ is the Gibbs free energy change of the stream as its pressure is reduced to that of the environment.

The proposed next step in the path for the stream to equilibrate with the environment is the reversible isothermal oxidation reaction at T_0 of the combustibles present in the stream utilizing the ambient air:

$$W_{\text{chemical}} = -\Delta G_{\text{chemical}} \tag{14}$$

The proposed final step in the path for the stream to equilibrate with the environment is the reversible isothermal expansion at T_0 of component i through the hypothetical reversible membrane to its partial pressure in the ambient air (i.e., as depicted in Fig. 1 by allowing the component to reversibly exchange through a selective membrane between the stream and a chamber, and similarly between the ambient air and a second chamber, the two chambers being connected by a turbo-expander operating reversibly between the two pressures):

$$W_{\text{concentration}} = -\Delta G_{\text{concentration}} \tag{15}$$

This work potential would be typically small with most current practical fuel cell systems, unless O_2 is used instead of air as the oxidant in which case it would allow accounting for the work required to separate O_2 from air. Similarly, in the case of a water electrolyzer, if O_2 is produced as a byproduct for sale, credit may be given to this stream. The other components considered for this type of work potential would be water vapor and carbon dioxide produced from the oxidation of the fuel or those present in the exhaust in the case of a fuel cell, although their contribution to the overall exergy may be quite small. The oxygen and nitrogen present in the exhaust of a fuel cell could also produce work by expansion but in the reverse direction, since a concentration gradient may exist for these components between the system and the environment (the concentration in the environment being typically higher). Such considerations would however provide impractical guidance for system improvements.

4. Simplified expression for efficiency

In many practical applications, the total exergy of the streams entering in the case of a fuel cell or leaving in the case of a water electrolyzer is predominantly due to the chemical energy contained in the stream. Furthermore if both Q_{in} and Q_{out} are small or if T_{in} tends to be near ambient temperatures and the thermal energy in the exhaust cannot be utilized for generating additional power, the expression for the second-law efficiency reduces to the following expressions:

For a fuel cell operating near ambient temperature:

$$\eta_{\text{II}} = \frac{W_{\text{out}}}{-\Delta G_R} \tag{16}$$

since $-\Delta G_R \sim \sum \chi_{\text{in}}$ for the oxidation reaction of the fuel, ΔG_R being the Gibbs free energy change for the reaction representing the maximum work that may be produced by the overall chemical reaction.

Or,

$$\eta_{\text{II}} = \frac{U_{\text{ACT}}}{U_{\text{REV}}} \tag{17}$$

For an electrolyzer operating near ambient temperature:

$$\eta_{\text{II}} = -\frac{\Delta G_R}{W_{\text{in}}} \tag{18}$$

since $-\Delta G_R \sim \sum \chi_{\text{out}}$ for the oxidation reaction of the product, e.g., H_2 in the case of a water electrolyzer, and ΔG_R being the Gibbs free energy change for the oxidation of the product representing the maximum work that may be produced by the overall chemical reaction.

Or,

$$\eta_{\text{II}} = \frac{\Delta G'_R}{W_{\text{in}}} \tag{19}$$

$$= \frac{U_{\text{REV}}}{U_{\text{ACT}}} \tag{20}$$

System	Chamber 1		Chamber 2	Environment
Stream containing Component i at Partial Pressure P_i	Pure Component i at Total Pressure P_i in Equilibrium with System	**Reversible Expander**	Pure Component i at Total Pressure P_{io} in Equilibrium with Environment	Ambient Air containing Component i at Partial Pressure P_{io}

Fig. 1. Reversible expansion of component after diffusion through membrane.

where U_{REV} is the reversible cell voltage required by the electrolyzer.

5. Conclusions/recommendations

The second-law efficiency for measuring and comparing the performance of electrochemical processes measures how close the process approaches a reversible process. It provides a true yardstick to measure the inefficiencies within the system. Furthermore, it accounts for the quality of thermal energy added to or removed from the system and thus provides a more consistent way of comparing different types of electrochemical devices. This consistency may allow better comparison of performance on a widespread basis, i.e., between groups working on distinct electrochemical systems. Other definitions of efficiency found in literature based on the first law of thermodynamics can generate efficiency values that are >100% for certain systems depending on whether the change in entropy for the overall chemical reaction involved in the process is positive or negative. Such efficiency values are misleading while making it difficult to compare processes that absorb or release significant quantities of thermal energy. The proposed use of the second-law efficiency which is within the frame work of the second law of thermodynamics, can reach 100% only in the limit of a reversible process and will always stay <100% whether the entropy change is positive or negative.

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