## Short Communication

# A novel approach for estimating the electrode kinetic parameters of gas-diffusion electrodes using the inflection point in steady-state current/potential data

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**Abstract**

A method is proposed for deriving electrode kinetic parameters (i.e., Tafel slopes, exchange-current densities and limiting currents) using the inflection point in steady-state current/potential data, without reaching the limiting-current region. The procedure is applied to the oxygen reduction reaction on a Nafion-bound platinized carbon electrode, a CoTMPP (cobalt tetramethoxyphenylporphyrine) catalyzed carbon electrode, and a pyrochlore oxide based electrode.

## Introduction

Fuel cells and metal/air batteries employ gas-diffusion electrodes for sustaining electrochemical reactions. The analysis of steady-state current/potential data on these gas-diffusion electrodes is imperative for deriving information on the charge-transfer, ohmic and mass-transfer parameters associated with these reactions. Nevertheless, the conventional methods of extracting such data are not always reliable. For example, recent attempts [1, 2] to derive these parameters for certain solid-polymer electrolyte fuel-cell electrodes are limited by the absence of mass-transfer corrections that caused a large disparity between the values of the electrolyte resistance obtained by the least-square fit and high-frequency measurements.

In this communication, a new method is presented for determining the electrode kinetic parameters of typical gas-diffusion electrodes for the reduction of oxygen, namely, a Nafion-bound platinized carbon electrode, a cobalt tetramethoxyphenyl-porphyrine (CoTMPP) catalyzed carbon electrode suitable for the solid-polymer-electrolyte fuel cell, and a pyrochlore oxide-based electrode. Unlike the conventional procedure [3], the present analysis does not require the steady-state current/potential data close to the limiting-current values that are usually prone to experimental errors

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arising from: (i) fluctuations in steady-state potential owing to evolution of gases; (ii) shielding of the electrode by gas bubbles that cause additional ohmic drop; (iii) interference from other reactions in the limiting-current range.

**Phenomenology**

Under cathodic Tafel conditions, the current-potential behaviour of a gas-diffusion electrode is described by:

$$E = E_{ocp} + 1/\alpha f \ln[i_{ocp}(i_{l,c} - |i|)/|i|i_{l,c}] - |i|R_u \quad (1)$$

where: $E$ = observed potential; $E_{ocp}$ = open-circuit potential; $i_{ocp}$ = current corresponding to $E_{ocp}$; $i$ = observed cathodic current; $i_{l,c}$ = cathodic-limiting current; $\alpha$ = cathodic transfer coefficient; $R_u$ = uncompensated resistance; $f = F/RT$ where $F$ is the Faraday constant, $R$ is the gas constant and $T$ is the temperature.

Equation (1) is sigmoidal in shape and possesses an inflection point at which the first derivative of potential with respect to the current, i.e., $(dE/d|i|)$, is maximum and, consequently, the second derivative is zero. Differentiating eqn. (1) with respect to current $i$ yields:

$$\frac{dE}{d|i|} = -\frac{1}{\alpha f}\frac{1}{|i|} - \frac{1}{\alpha f}\frac{1}{(i_{l,c} - |i|)} - R_u \quad (2)$$

On further differentiation, eqn. (2) becomes:

$$\frac{d^2E}{d|i|^2} = \frac{1}{\alpha f}\frac{1}{|i|^2} - \frac{1}{\alpha f}\frac{1}{(i_{lc} - |i|)^2} \quad (3)$$

At the inflection point, $i = i_{inf}$, $d^2E/d|i_{inf}|^2 = 0$ and, consequently:

$$\frac{1}{\alpha f|i_{inf}|^2} = \frac{1}{\alpha f}\frac{1}{(i_{lc} - |i_{inf}|)^2} \quad (4)$$

or:

$$i_{lc} = 2|i_{inf}| \quad (5)$$

Thus, the limiting current, $i_{lc}$, can be obtained by determining the value of the current at the inflection point which corresponds to the maximum in the plot of $dE/d|i|$ versus $1/|i|$.

After obtaining $i_{lc}$, the other kinetic parameters are obtained from eqn. (2) by recasting it in the following form:

$$\frac{dE}{d|i|} = -\frac{1}{\alpha f}\frac{i_{lc}}{|i|(i_{lc} - |i|)} - R_u \quad (6)$$

The plot of $dE/d|i|$ versus $i_{lc}/|i|(i_{lc} - |i|)$ leads to a straight line with an intercept $= -R_u$ and a slope $= -1/\alpha f$. The value of $i_{ocp}$ is obtained by substituting the values of $R_u$, $\alpha$ and $i_{lc}$ in eqn. (1).

**Experimental**

$Bi_2Ru_2O_7$ pyrochlore oxide was prepared by heating a mixture of the respective oxides in air at 1073 K for 12 h. The electrode substrate comprising the pyrochlore

oxide, dispersed in cyclohexane and an optimum quantity of (16 wt.%) of Fluon GP2 PTFE (polytetrafluoroethene) suspension, was mixed by agitation in an ultrasonic bath. The resulting mass was dried in an air oven at 100 °C and the electrodes were prepared by cold compacting the hydrophobized mass under a hydraulic press at an optimum pressure of 180 kg $cm^{-2}$ for 225 s.

Nafion-bound carbon electrodes were prepared by sand-witching the treated Vulcan XC-72 carbon-containing platinum (or CoTMPP) catalyst mixed with PTFE binder (Fluon GP2, ICI) between a Nafion film and platinum gauge under a compaction load of a 150 kg $cm^{-2}$, as described elsewhere [4]. The electrodes were subjected to galvanostatic polarization for cathodic reduction of oxygen in a three-electrode cell.

## Results and discussion

The steady-state current/potential data obtained galvanostatically for the cathodic reduction of oxygen on a $Bi_2Ru_2O_7$ electrode in 6 M KOH at 27 °C is shown in

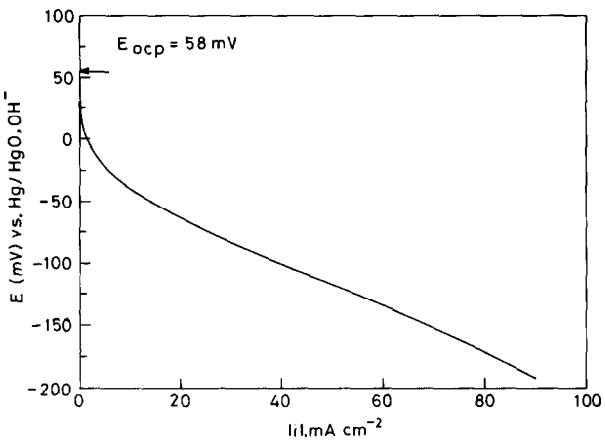


Fig. 1. Steady-state current/potential data for cathodic reduction of oxygen on pyrochlore electrode in 6 M KOH.

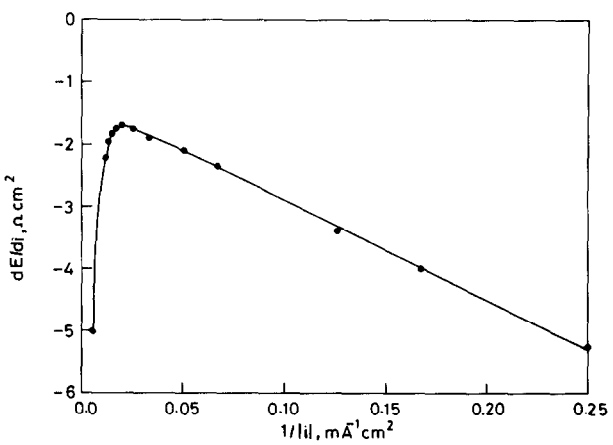


Fig. 2. Plot of $dE/d|i|$ vs. $1/|i|$ for curve in Fig. 1.

Fig. 1. The corresponding $dE/d|i|$ versus $1/|i|$ plot is given in Fig. 2. From Fig. 2, the current at the inflection point, which corresponds to the maximum of this plot is identified and limiting current value is obtained from eqn. (5). Subsequently, the value of $R_u$ and $\alpha$ are obtained from the plot of $dE/d|i|$ versus $i_{lc}/|i|(i_{lc}-|i|)$ shown in Fig. 3. The resulting values of $R_u$, $b_c$ (where $b_c$, the Tafel slope, is given by $2.303/\alpha f$), $i_{lc}$ and $i_o$ (where $i_o$ is the current corresponding to the reversible potential for oxygen reduction in the medium) are 1.7 $\Omega$ cm$^2$, 28 mV, 100 mA cm$^{-2}$ and $1.05\times10^{-17}$ A cm$^{-2}$, respectively.

The steady-state current/potential data in semi-log plot is shown in Fig. 4. It clearly reflects the presence of a diffusion-controlled reaction. After ohmic and mass-transfer corrections, the plot of $E$ versus $\log |i|i_{lc}/(i_{lc}-|i|)$ is presented in Fig. 5. A well-defined Tafel line over about two decades is obtained. From this plot, the values of $i_o$ and $b_c$ are calculated to be $1\times10^{-17}$ A cm$^{-2}$ and 28 mV, respectively. These values are in agreement with those obtained from the plot in Fig. 3.

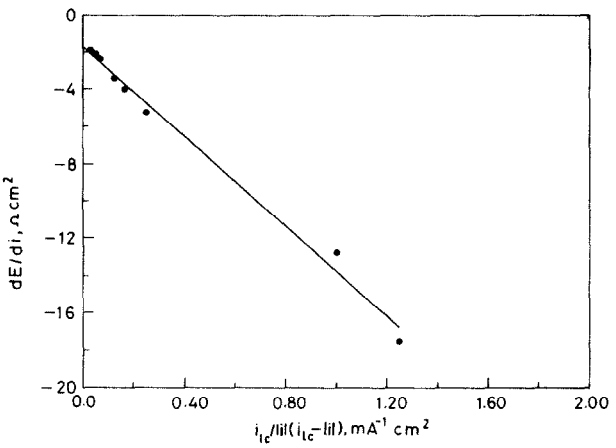


Fig. 3. Plot of $dE/d|i|$ vs. $i_{lc}/|i|(i_{lc}-|i|)$ for curve in Fig. 1.

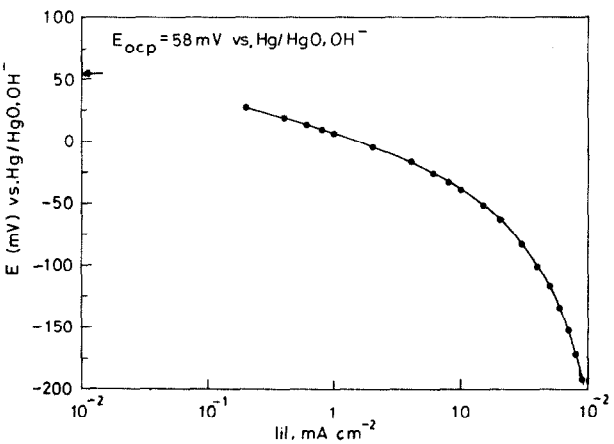


Fig. 4. Plot of $E$ vs. $\log |i|$ for curve in Fig. 1.

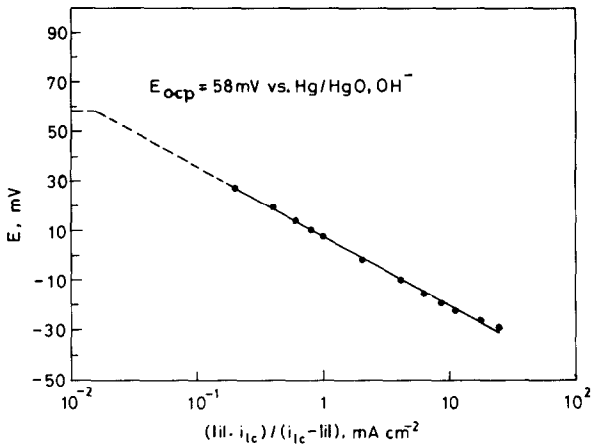


Fig. 5. Plot of $E$ vs. log $|i|i_{lc}/(i_{lc}-|i|)$ for curve in Fig. 1.

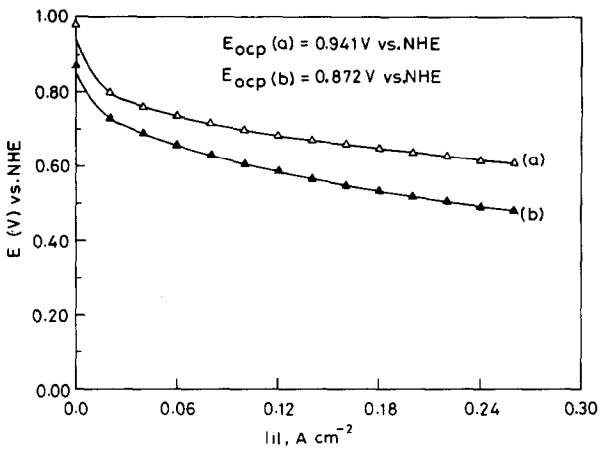


Fig. 6. Steady-state current/potential data for cathodic reduction of oxygen on: (a) Pt/carbon electrode; (b) CoTMPP electrode Nafion-bound solid electrolyte.

The steady-state current/potential data for the Nafion-bound carbon electrodes containing platinum and CoTMPP are given in Fig. 6. It is noteworthy that, unlike the previous case, the current densities do not reach a limiting-current region. Accordingly, eqn. (1) could be written as:

$$E = E_{ocp} + 1/\alpha f \ln(i_{ocp}/|i|) - |i|R_u \quad (7)$$

and hence a plot of $dE/d|i|$ versus $1/|i|$ will be a straight line with slope and intercept values of $-1/\alpha f$ and $-R_u$, respectively. Such plots for the data in Fig. 6 are given in Fig. 7. The values of the ohmic and charge-transfer components, as derived from these data for Nafion-bound electrodes with platinized carbon or CoTMPP coated carbon, are listed in Table 1.

## Conclusions

The present method of deriving electrode kinetic parameters, namely, Tafel slope, exchange-current density and limiting current, from the steady-state current/potential

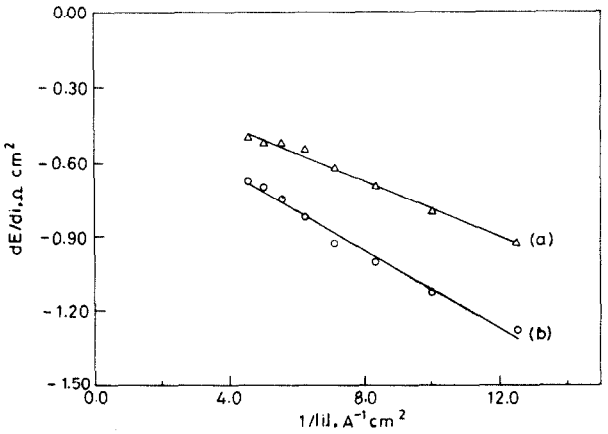


Fig. 7. Plot of $(dE/d|i|)$ vs. $1/|i|$ for curves in Fig. 6.

TABLE 1

Ohmic and charge-transfer components for Nafion-bound electrodes with platinized carbon or CoTMPP catalyzed carbon substrates

| Electrode type | Tafel slope $b_c$ (mV) | Uncompensated resistance $R_u$ ($\Omega$ cm$^2$) | Exchange current $i_o$ ($\times 10^{-5}$ A cm$^{-2}$) |
|---|---|---|---|
| Pt/carbon | 128 | 0.23 | 1.05 |
| CoTMPP/carbon | 179 | 0.23 | 4.74 |

data is superior to the conventional method as it does not require the limiting-current value. It is advanced that this method would be especially useful for determining electrode kinetic parameters of the gas-diffusion electrodes employed in fuel cells and metal/air batteries.

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## References

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