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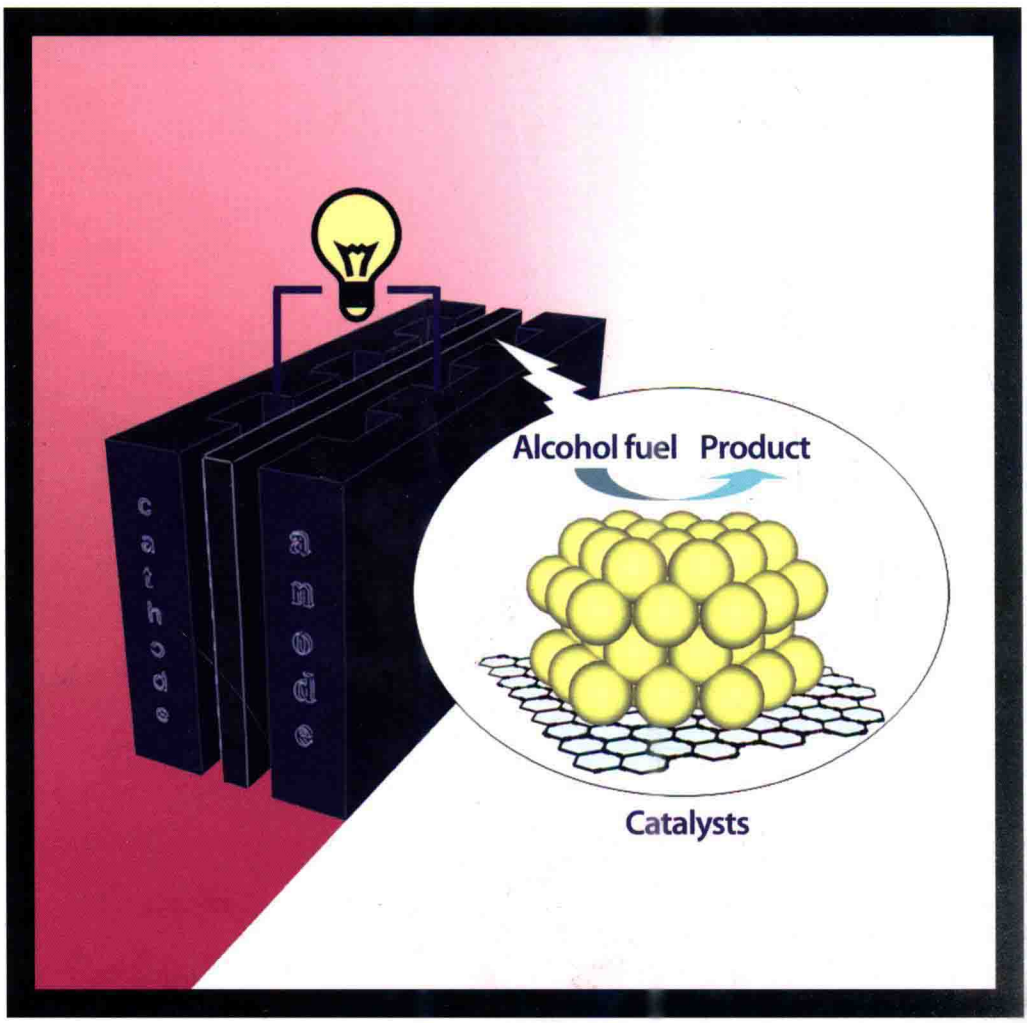
Edited by Z. X. Liang and T. S. Zhao

Catalysts for Alcohol-Fuelled Direct Oxidation Fuel Cells



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Preface

Energy and environment issues are of paramount importance to achieve the sustainable development of our society. Alcohol-fuelled direct oxidation fuel cells (DOFCs), as a clean and highly efficient energy harvesting engine, have attracted intensive research activities over recent decades. Catalysts are the heart material that determines the performance of DOFCs. The rapid advances in electrocatalysts, particularly nano-sized ones, have left current information available only in scattered journals. To be truly useful to both present and future researchers in the field, this book is intended to devote an insightful review of the reaction nature, systematically summarize the recent advances in nanocatalysts, and convey a more global perspective. Contributions by leading experts will serve as a central source of reference for the fundamentals and applications of the electrocatalysts, establishing the state of the art, disseminating the latest research discoveries, and providing a potential textbook to senior undergraduate and graduate students.

Chapter 1 provides an informative summary on the electrocatalysis of the alcohol oxidation reactions and the platinum-based electrocatalysts. Chapters 2–6 deal with the recent advances in both the fundamental understanding and the material science in DOFCs. Special emphasis is placed on the newly emerging nanocatalysts developed over the past several years, including the novel nanostructured electrocatalysts, the gold-leaf-based nanocatalysts, the palladium-based nanocatalysts, bioelectrocatalysts, and correlation of the "structure–activity" relationship as well. Based on the discussion, the challenges and perspectives of the nanocatalysts in alcohol-fuelled DOFCs are extensively discussed in Chapter 7. In addition to typical alcohol oxidation reactions, recent developments of nanocatalysts for other fuel (formic acid, borohydride, sugars, *etc.*) oxidation reactions are also included in this book.

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The editorial board expresses their appreciation to the contributing authors, who have set the high standards for *Catalysts for Alcohol-Fuelled Direct Oxidation Fuel Cells*. Last, but not least, the editors acknowledge the efforts of the professional staff at the Royal Society of Chemistry for providing invaluable editorial assistance.

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CHAPTER 1

Electrocatalysis of Alcohol Oxidation Reactions at Platinum Group Metals

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1.1 Introduction

Electrocatalysis, *i.e.* the heterogeneous catalysis of electrochemical reactions occurring at the electrode/electrolyte interface, has mainly concerned technological investigations related either to energy storage (*e.g.* water electrolysis) or to energy conversion (*e.g.* fuel cells).[1,2] However, except for the hydrogen electrode, which is now well known, and the oxygen electrode, which has been extensively studied, other electrodes of practical interest, such as soluble fuel electrodes, need much more investigation. Among them, alcohol electrodes are particularly suitable for use in a direct oxidation fuel cell (DOFC) because of several favourable features, such as a high theoretical energy density (4–9 kWh kg^{-1} compared to 33 kWh kg^{-1} for molecular hydrogen) and a great facility of handling.

Moreover, alcohols, which may be produced from the biomass, are very interesting fuels due to a lot of advantages: high solubility in aqueous

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electrolytes, relatively high reactivity, ease of storage and supply, low toxicity (except for methanol). They can be directly electro-oxidized in a direct alcohol fuel cell (DAFC).This explains why many fundamental investigations were undertaken in the last three decades on the electrochemical oxidation of several alcohols: methanol,[3–5] ethanol,[6–8] ethylene glycol,[6,9] glycerol,[10] propanol[11] and butanol,[12,13] and also on related compounds: formic acid,[14–16] formaldehyde,[17] carbon monoxide,[18] *etc.* Until now, the most promising and most studied fuels for application in a DOFC, with the direct oxidation of the organic molecule, are alcohols such as methanol and ethanol.

However, a lot of electrocatalytic problems still arise due to the relative complexity of the reaction mechanisms. These include the effect of the nature of the reaction products, the structure of the adsorbed intermediates, the nature and structure of the electrode material, the molecular structure of the organic compounds, the pH and the anions of the supporting electrolyte, and the role of the water adsorption residues.

Furthermore, the catalyst structure, such as the particle size, the composition and the degree of alloying, are also of great importance, since most of the alcohol oxidation reactions are structure sensitive and because it is of great interest to reduce the platinum group metal loading (either by metal dispersion or by synthesis of multimetallic catalysts) in order to reduce the cost of the DAFC system. These topics will be illustrated mainly with results obtained in this laboratory.

1.2 Thermodynamics and Kinetics of Alcohol Oxidation Reactions

In a DOFC the total electro-oxidation to CO_2 of an aliphatic oxygenated compound C_xH_yO containing one oxygen atom (mono-alcohols, aldehydes, ketones, ethers, *etc.*) involves the participation of water (H_2O) or of its adsorbed residue (OH_{ads}) provided by the cathodic reaction (electro-reduction of dioxygen).

The overall electro-oxidation reaction in acid medium to reject the carbon dioxide produced can thus be written as follows:

$$C_xH_yO + (2x-1)H_2O \rightarrow xCO_2 + nH^+ + ne^- \qquad (1.1)$$

with $n = 4x + y - 2$. Such an anodic reaction is very complicated from a kinetics point of view since it involves multielectron transfers and the presence of different adsorbed intermediates and several reaction products and by-products. However, from thermodynamic data it is easy to calculate the reversible anode potential, the cell voltage under standard conditions, the theoretical energy efficiency and the energy density.

1.2.1 Thermodynamic Data

According to reaction (1.1) the standard Gibbs energy change $-\Delta G_1^\circ$, allowing calculation of the standard anode potential, $E_1^\circ = \dfrac{-\Delta G_1^\circ}{nF}$, can be evaluated from the standard energy of formation ΔG_i^f of reactant i:

$$-\Delta G_1^\circ = x\Delta G^f_{CO_2} - \Delta G^f_{C_xH_yO} - (2x-1)\Delta G^f_{H_2O} \tag{1.2}$$

In the cathodic compartment the electro-reduction of oxygen occurs, as follows:

$$^1/_2O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{1.3}$$

with $\Delta G_2^\circ = \Delta G^f_{H_2O} = -237.1$ kJ mol^{-1}, leading to a standard cathodic potential, E_2°:

$$E_2^\circ = E^\circ_{O_2} = -\frac{\Delta G_2^\circ}{2F} = \frac{237.1 \times 10^3}{2 \times 96485} = 1.229 \text{ V } \textit{vs.} \text{ SHE} \tag{1.4}$$

where SHE is the standard hydrogen electrode, acting as a reference electrode.

In the fuel cell the electrical balance corresponds to the complete combustion of the organic compound in the presence of oxygen, as follows:

$$C_xH_yO + (x + \frac{y}{4} - \frac{1}{2})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \tag{1.5}$$

with $\Delta G_r^\circ = (2x + \frac{y}{2} - 1)\Delta G_2^\circ - \Delta G_1^\circ = x\Delta G^f_{CO_2} + \frac{y}{2}\Delta G^f_{H_2O} - \Delta G^f_{C_xH_yO}$, leading to the equilibrium standard cell voltage:

$$E^\circ_{eq} = -\frac{\Delta G_r^\circ}{nF} = -\frac{\Delta G_2^\circ}{2F} + \frac{\Delta G_1^\circ}{nF} = E_2^\circ - E_1^\circ = E^\circ_{O_2} - E^\circ_{alcohol} \tag{1.6}$$

Then it is possible to evaluate the specific energy W_e in kWh kg^{-1}:

$$W_e = \frac{(-\Delta G_r^\circ)}{3600\ M} \tag{1.7}$$

with M the molecular mass of the compound. Knowing the enthalpy change ΔH° from thermodynamic data:

$$\Delta H_r^\circ = (2x + \frac{y}{2} - 1)\Delta H_2^\circ - \Delta H_1^\circ = x\Delta H^f_{CO_2} + \frac{y}{2}\Delta H^f_{H_2O} - \Delta H^f_{C_xH_yO} \tag{1.8}$$

one may calculate the reversible energy efficiency under standard conditions:

$$\varepsilon_{rev} = \frac{\Delta G_r^\circ}{\Delta H_r^\circ} \tag{1.9}$$

For the oxidation of methanol and ethanol, the corresponding equations are:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \qquad E^\circ_{MeOH} = 0.016 \text{ V } \textit{vs.} \text{ SHE} \qquad (1.10)$$

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \qquad E^\circ_{EtOH} = 0.085 \text{ V } \textit{vs.} \text{ SHE} \qquad (1.11)$$

whereas the electro-reduction reaction of molecular oxygen occurs at the cathode:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^\circ_{O_2} = 1.229 \text{ V } \textit{vs.} \text{ SHE} \qquad (1.12)$$

where E°_i are the standard electrode potentials *vs.* SHE.

This corresponds to the overall combustion reaction of alcohols in oxygen:

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O \qquad E^\circ_{O_2/MeOH} = 1.213 \text{ V} \qquad (1.13)$$

$$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \qquad E^\circ_{O_2/EtOH} = 1.145 \text{ V} \qquad (1.14)$$

where the cell voltages are calculated under standard conditions.

For higher alcohols, such as *n*-propanol, taken as an example, the following calculations can be made:

$$C_3H_7OH + 5H_2O \rightarrow 3CO_2 + 18H^+ + 18e^- \qquad (1.15)$$

$$\begin{aligned} -\Delta G^\circ_1 &= 3\Delta G^f_{CO_2} - \Delta G^f_{C_3H_7OH} - 5\Delta G^f_{H_2O} \\ &= -3 \times 394.4 + 168.4 + 5 \times 237.1 = 171 \text{ kJ mol}^{-1} \end{aligned} \qquad (1.16)$$

$$E^\circ_1 = -\frac{\Delta G^\circ_1}{18F} = \frac{171 \times 10^3}{18 \times 96485} = 0.098 \text{ V } \textit{vs.} \text{ SHE} \qquad (1.17)$$

$$C_3H_7OH + 9/2O_2 \rightarrow 3CO_2 + 4H_2O \qquad (1.18)$$

$$\begin{aligned} \Delta G^\circ_r &= 9\Delta G^\circ_2 - \Delta G^\circ_1 = 3\Delta G^f_{CO_2} + 4\Delta G^f_{H_2O} - \Delta G^f_{C_3H_7OH} \\ &= -3 \times 394.4 - 4 \times 237.1 + 168.4 = -1963 \text{ kJ mol}^{-1} \end{aligned} \qquad (1.19)$$

The standard cell voltage is thus:

$$\begin{aligned} E^\circ_{eq} &= -\frac{\Delta G^\circ_r}{18F} = \frac{1963 \times 10^3}{18 \times 96485} = \frac{237.1 \times 10^3}{2 \times 96485} - \frac{171 \times 10^3}{18 \times 96485} \\ &= 1.229 - 0.098 = 1.131 \text{ V} \end{aligned} \qquad (1.20)$$

and the specific energy is:

$$W_e = \frac{1963}{3600 \times 60} = 9.09 \text{ kWh kg}^{-1} \tag{1.20a}$$

The enthalpy change of reaction (1.18) is:

$$\Delta H_r^\circ = -3 \times 395.5 - 4 \times 285.8 + 302.6 = -2027 \text{ kJ mol}^{-1} \tag{1.21}$$

so that the reversible energy efficiency is :

$$\varepsilon_{rev} = \frac{\Delta G_r^\circ}{\Delta H_r^\circ} = \frac{1963}{2027} = 0.968 \tag{1.22}$$

Similar calculations can be made with many oxygenated fuels, including polyols (ethylene glycol, glycerol), propargyl alcohol, ethers and polyethers [dimethyl ether, CH_3OCH_3, ethyl methyl ether, $CH_3OC_2H_5$, diethyl ether, $C_2H_5OC_2H_5$, dimethoxymethane, $(CH_3O)_2CH_2$, trimethoxymethane, $(CH_3O)_3CH$, trioxane, $(CH_2O)_3$].

The energy density of the fuel, W_e, the cell voltage of the cell at equilibrium, E°_{eq}, and the reversible energy efficiency of the cell, ε_{rev}, for several alcohols can be calculated under standard conditions (25 °C, liquid phase). The results are summarized in Table 1.1.

For all oxygenated compounds listed in Table 1.1, the cell voltage varies from 1.2 to 1.0 V, which is very similar to that of a hydrogen/oxygen fuel cell (E°_{eq} = 1.23 V). The energy density varies between half to one of that of gasoline (10–11 kWh kg^{-1}), so these compounds are good alternative fuels to hydrocarbons. Furthermore, the reversible energy efficiency ε_{rev} is close to 1, while that of the H_2/O_2 fuel cell is 0.83 at 25 °C (standard conditions). From these data, it appears that amongst the mono-alcohols, methanol and ethanol lead to higher cell voltages and reversible energy efficiency under standard conditions.

Table 1.1 Thermodynamic data associated with the electrochemical oxidation of some alcohols (under standard conditions).

Fuel	$\Delta G_1^\circ/kJ\ mol^{-1}$	E_1°/V vs. *SHE*	$\Delta G_r^\circ/kJ\ mol^{-1}$	E°_{cell}/V	$W_e/kWh\ kg^{-1}$	$\Delta H_r^\circ/kJ\ mol^{-1}$	ε_{rev}
CH_3OH	−9.3	0.016	−702	1.213	6.09	−726	0.967
C_2H_5OH	−97.3	0.084	−1325	1.145	8.00	−1367	0.969
C_3H_7OH	−171	0.098	−1963	1.131	9.09	−2027	0.968
n-C_4H_9OH	−409	0.177	−2436	1.052	9.14	−2676	0.910
CH_2OH–CH_2OH	−25.5	0.026	−1160.8	1.203	5.20	−1189	0.976
CH_2OH–$CHOH$–CH_2OH	1	−0.01	−1661.6	1.230	5.02	−1650	0.993

1.2.2 Kinetics Problems

The electro-oxidation of aliphatic oxygenated compounds, even the simplest one, *i.e.* methanol, involves the transfer of many electrons ($n = 6$ for methanol). The reaction mechanism is thus complex, the oxidation reaction occurring through many successive and parallel paths involving many adsorbed intermediates and by-products. The oxidation reaction needs a convenient electrocatalyst to increase the reaction rate and to modify the reaction pathway in order to reach more rapidly the final step, *i.e.* the production of carbon dioxide. The relative slowness of the reaction, and the difficulty to break the C–C bond at low temperatures (25–80 °C), lead to high anodic overvoltages η_a, which will greatly reduce the operating cell voltage (Figure 1.1).

Thus, the practical electrical efficiency of a fuel cell is dependent on the current that is delivered by the cell and is lower than that of the reversible efficiency due to the irreversibility of the electrochemical reactions involved at the electrodes. The practical efficiency of a fuel cell can be expressed as follows:

$$\varepsilon_{cell} = \frac{n_{exp} \times F \times E(j)}{-\Delta H_r^\circ} = \frac{nFE_{eq}^\circ}{(-\Delta H_r^\circ)} \times \frac{E(j)}{E_{eq}^\circ} \times \frac{n_{exp}}{n} = \varepsilon_{rev} \times \varepsilon_E \times \varepsilon_F \qquad (1.23)$$

with the cell voltage $E(j) = E^\circ_{eq} - (|\eta_a| + |\eta_c| + R_e j)$ at a current density j and R_e the electrolyte and interfacial specific resistances.

From eqn (1.23) it follows that the increase of the practical fuel cell efficiency can be achieved by increasing the voltage efficiency ($\varepsilon_E = E(j)/E^\circ_{eq}$) and the faradic efficiency ($\varepsilon_F = n_{exp}/n$), the reversible yield being fixed by the thermodynamic data.

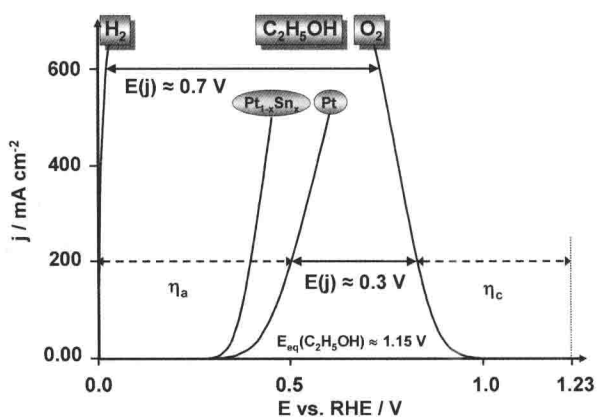

Figure 1.1 Current density (j) *vs.* electrode potential (E) curves for H_2 and EtOH electro-oxidation at different Pt-based catalytic anodes, and oxygen electro-reduction at a Pt cathode.