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Effect of junction potential on the EMF of bielectrolyte solid-state sensors

Fushen Li, Hui Xia, Ling Wang, Yanhong Zhang, and Lifen Li

Materials Science and Engineering School, University of Science and Technology Beijing, Beijing 100083, China

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Abstract: The EMF (electromotive force) expressions of bielectrolyte solid-state sensors derived from classical thermodynamics are not rigorous. They are only applicable in some special situations. In order to expand their applicable scope, they should be derived from irreversible thermodynamics theory. There is a junction potential term in the EMF equations of double solid electrolyte sensors derived from irreversible thermodynamics. The junction potential involves the ion transference numbers and the electron transference numbers of two kinds of solid electrolytes. When the transference numbers of reaction ions in the two solid electrolytes equal 1 only, the junction potential term is zero and two types of EMF equations become the same.

Key words: solid electrolyte; sensor; electromotive force; junction potential; transference number

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1 Introduction

Solid electrolyte sensors could be divided into four types: (1) sensors whose solid electrolyte conductive ions are the components for measuring; (2) sensors whose polyphase-compound solid electrolytes contain the activity-constant resultants of conductive ions and components for measuring; (3) sensors whose auxiliary electrodes contain resultants of conductive ions and components for measuring; (4) double solid electrolyte sensors.

Compared with other kinds of solid electrolye sensors, double solid electrolyte sensors, which have been developed in recent years, have the following merits: (1) simple construction and easy to produce in bulk with film technique; (2) easy to microminiaturize and pluralize; (3) no need of reference electrode and having no seal problems; (4) low cost. Therefore this kind of sensors has become one of the major research fields of solid electrolyte gas sensors and has a bright prospect of development [1-5].

2 CO_2 gas sensor based on solid electrolytes NASICON and YSZ

For example, the sensor based on the solid electrolyte NASICON ($Na_3Zr_2Si_2Po_{12}$) and YSZ (yttria stabilized zirconia) is a CO_2 gas. The solid electrolyte NASICON is a conductor of sodium ion, and the YSZ is a conductor of oxygen ion. The cell construction could be expressed as

$$\mathrm{Pt}|\mathrm{CO_2,O_2}|\mathrm{Na_2CO_3}|\mathrm{NASICON}|\mathrm{YSZ}|\mathrm{O_2,CO_2}|\mathrm{Pt}.$$

The reactions that take place in this system are considered as

Anode: $Na_2CO_3=2Na^++\frac{1}{2}O_2+CO_2+2e$,

Cathode: $\frac{1}{2}O_2+2e=O^{2-}$.

At the junction of NASICON and YSZ: $2Na^++O^{2-}=Na_2O$(in NASICON).

Overall reaction:

$Na_2CO_3=Na_2O$(in NASICON)$+CO_2$.

According to classical thermodynamics, the relational expression of CO_2 partial pressure and the cell's EMF is given by the Nernst equation

$$E=-\frac{\Delta G^{\circ}}{2F}-\frac{RT}{2F}\ln[a_{\mathrm{Na_2O}}\frac{P_{\mathrm{CO_2}}}{P^{\ominus}}] \quad (1)$$

From the cell expression above, it can be seen that the sensor is based on double solid electrolyte and has no reference electrodes. The electrode seal problem is nonexistent. This is because the two electrodes are ex-

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Corresponding author: Fushen Li, **E-mail:** lifsh_ustb@163.com

posed to the same test gas. The simple structure of this kind of sensors leads themselves to highly efficient and low-cost bulk production using thin film technology.

However there is a theoretical problem with this EMF equation of the cell. The EMF (electromotive force) equation (1) is correct only when sodium ion (Na^+) and oxygen ion (O^{2-}) transport at the solid junction at exactly the same rate. That is to say, the transference numbers of Na^+ and O^{2-} are both equal to 1. If the tansference numbers are different, the charge can accumulate at the solid junction (phase boundary) and produce a junction potential. The EMF equation would not be accurate unless the junction potential across the two solid electrolye is taken into consideration.

3 Calculation of the EMF based on the equations of irreversible thermodynamics

With the help of irreversible thermodynamics, Carl Wagner deduced the general EMF expression when junction potential exists [6]. The expression of the potential difference across boundary between two phases is

$$\Delta\varphi(\nu,\nu+1)=\varphi'(\nu+1)-\varphi''(\nu)=-\frac{\mu'_i(\nu+1)-\mu''_i(\nu)}{Z_iF} \tag{2}$$

The expression of the electrical potential difference in a single phase ν is

$$\Delta\varphi=\varphi''(\nu)-\varphi'(\nu)=-\frac{1}{F}\sum_i\int_{\mu'_i(\nu)}^{\mu''_i(\nu)}t_i^*\mathrm{d}\mu_i \tag{3}$$

Then one can obtain the total EMF of a cell by adding potential differences across phase boundaries according to equation (2) and the potential difference of a single phase according to equation (3).

Several cases are discussed as follows.

(a) If both electrodes are reversible for the same cation, it is expedient to choose this cation as the master cation A. For example, consider the cell

$$\mathrm{Pt(1)}\underset{\mathrm{a}}{|}\mathrm{Alloy(2)}\underset{\mathrm{b}}{|}\mathrm{Electrolyte(3)}\underset{\mathrm{c}}{|}\mathrm{Alloy(4)}\underset{\mathrm{d}}{|}\mathrm{Pt(5)}$$

with Pt leads (1) and (5), alloy phases (2) and (4) each of uniform composition, which represent electrodes reversible for cation A. There is chemical potential gradient in electrolyte phase (3). The EMF of the cell can be calculated as

$$E=\varphi(5)-\varphi(1).$$

Then one may use equation (2) for i=electron in order to calculate the phase boundary potential difference between Pt (1) and alloy (2), and between alloy (4) and Pt (5). Further, one may use equation (2) for i=cation A in order to calculate the potential difference across the phase boundary b between alloy (2) and electrolyte (3), and the phase boundary c between electrolyte (3) and alloy (4). Then one can use equation (3) to calculate the potential difference across the single phase of electrolyte (3). Therefore the EMF equal to the potential difference between Pt leads (5) and (1) is calculated as the sum of the various potential differences across phase boundaries and the potential difference across the single phase of electrolyte (3). The EMF expression through reduction is

$$E=-\frac{1}{F}[\bar{\mu}_{[\mathrm{A}]}(4)-\bar{\mu}_{[\mathrm{A}]}(2)+\sum_\alpha\int t_\alpha\mathrm{d}\bar{\mu}_{\alpha\mathrm{B}}-\sum_\alpha\int t_\alpha\mathrm{d}\bar{\mu}_{\mathrm{AB}}-\sum_{\beta\neq e}\int t_\beta\mathrm{d}\bar{\mu}_{\mathrm{A}\beta}-\int t_e\mathrm{d}\bar{\mu}_{[\mathrm{A}]}+\sum_\gamma\int t_\gamma^*\mathrm{d}\mu \tag{4}$$

where $\bar{\mu}_{[\mathrm{A}]}(2)$ and $\bar{\mu}_{[\mathrm{A}]}(4)$ are the chemical potentials per equivalent of component A at the left-hand and the right-hand electrode, respectively, α indicates the cation, β is the anion, B represents the master anion, γ is the neutral component. All integrals are to be extended over the entire cell.

(b) If both electrodes are reversible for the same anion, it is expedient to choose this anion as the master anion B. For example, for the cell

$$\frac{\mathrm{Pt}}{(1)}\Bigg|\frac{\mathrm{nonmetal[B]}(\mu^{(2)}_{[\mathrm{B}]})}{(2)}\Bigg|\frac{\mathrm{electrolyte}}{(3)}\Bigg|\frac{\mathrm{nonmental[B]}(\mu^{(4)}_{[\mathrm{B}]})}{(4)}\Bigg|\frac{\mathrm{Pt}}{(5)}.$$

One get

$$E=-\frac{1}{F}[\bar{\mu}_{[\mathrm{B}]}(2)-\bar{\mu}_{[\mathrm{B}]}(4)+\sum_\alpha\int t_\alpha\mathrm{d}\bar{\mu}_{\alpha\mathrm{B}}+\sum_{\beta\neq e}\int t_\beta\mathrm{d}\bar{\mu}_{\mathrm{AB}}-\sum_{\beta\neq e}\int t_\beta\mathrm{d}\bar{\mu}_{\mathrm{A}\beta}+\int_{(3)'}^{(3)'}t_e\mathrm{d}\bar{\mu}_{[\mathrm{B}]}+\sum_\gamma\int t_\gamma^*\mathrm{d}\mu_\gamma] \tag{5}$$

where $\bar{\mu}_{[\mathrm{B}]}(2)$ and $\bar{\mu}_{[\mathrm{B}]}(4)$ are the chemical potentials per equivalent of element B at the left-hand and the right-hand electrode, respectively. All integrals are to be extended over the entire cell.

4 Deduction of EMF equation of CO_2 bielectrolyte solid-state sensor

The cell construction of the sensor is as follows.

$$\mathrm{Pt}|\mathrm{CO_2,O_2}|\mathrm{Na_2CO_3}|\mathrm{NASICON(Na_2O)}|\mathrm{YSZ}|\mathrm{O_2,CO_2}|\mathrm{Pt} \tag{6}$$

and it can be consider that the cell is composed of a new cell

$$\frac{\mathrm{Pt}}{(1)}\Bigg|\frac{\mathrm{CO_2,O_2}|\mathrm{Na_2O}}{(2)}\Bigg|\frac{\text{'NASICON(Na}_2\text{O)"}|\text{'YSZ"}}{(3)}\Bigg|\frac{\mathrm{CO_2,O_2}}{(4)}\Bigg|\frac{\mathrm{Pt}}{(5)} \tag{7}$$

and a reaction of Na_2CO_3 decomposition

$$Na_2CO_3=Na_2O+CO_2 \qquad (8)$$

Then the ΔG of the original cell (6) is the sum of the ΔG_1 of the new cell (7) and the ΔG_2 of Na_2CO_3 decomposition reaction (8)

$$\Delta G = \Delta G_1 + \Delta G_2 .$$

According to thermodynamics equation $\Delta G = -nEF$, one get

$$E = -\Delta G_1 / nF + \Delta G_2 / nF ,$$

and $E = E_1 + E_2$.

where E_1 is the EMF of the new cell (7) and E_2 can be calculated from the Na_2CO_3 decomposition reaction (8).

First, consider the new cell's reactions that take place in this system.

Anode: $Na_2O=2Na^+ + \frac{1}{2}O_2+2e$,

and $2Na^+ + O^{2-}=Na_2O(N)$.

The total anode reaction is

$$Na_2O+O^{2-}=Na_2O(N)+\frac{1}{2}O_2+2e .$$

Cathode: $\frac{1}{2}O_2+2e=O^{2-}$.

Overall reaction: $Na_2O=Na_2O(N)$.

where superscripts ' and " denote quantities at the left-hand and the right-hand phase boundary respectively, and (N) denotes the phase NASICON. One can see Pt leads (1) and (5) and gas phases (2) and (4) are of the same uniform composition, which represent electrodes reversible for anion B. There is a solid junction between NASICON (Na^+ conductor) and YSZ (O^{2-} conductor). Both electrodes are reversible for O^{2-} because the reactions of anode and cathode are both reactions in which oxygen gets or loses electrons. Therefore one shall apply equation (5) to deduce the EMF equation of the new cell (7).

For the new cell (7), there are Na^+ and electron transportations in NASICON and there are O^{2-} and electron transportations in YSZ. The two electrodes of this cell are under the same oxygen partial pressure, so $\bar{\mu}''_{[B]}$ is the same with $\bar{\mu}'_{[B]}$ and the item $\bar{\mu}''_{[B]} - \bar{\mu}'_{[B]}$ of equation (5) is equal to zero. In the whole cell, there is only one single anionic component O^{2-}, so β=B=O^{2-} and the term $\int\left(\sum_{\beta\neq e} t_\beta\right)\mathrm{d}\bar{\mu}_{AB} - \sum_{\beta\neq e}\int t_\beta \mathrm{d}\bar{\mu}_{A\beta}$ in equation (5) is equal to zero. In addition, there is no transport of neutral components. One could then rewrite equation (5) as

$$\begin{aligned} E_1 &= -\frac{1}{F}[\int t_{Na^+}\mathrm{d}\bar{\mu}_{Na_2O}(N) + \int_{(N)}^{(Y)'} t_e \mathrm{d}\bar{\mu}_{[O_2]} \\ &= -\frac{1}{F}[\int t_{Na^+}\mathrm{d}\bar{\mu}_{Na_2O}(N) + (1-t_{Na^+})(\bar{\mu}''_{[O_2]} - \bar{\mu}'_{[O_2]})(N) + \\ &\quad (1-t_{O^{2-}})(\bar{\mu}''_{[O_2]} - \bar{\mu}'_{[O_2]})(Y)] \end{aligned} \qquad (9)$$

where (N) denotes the phase NASICON and (Y) denotes the phase YSZ. In addition

$$\bar{\mu}'_{O_2}(N) = \bar{\mu}''_{O_2}(Y),\ \bar{\mu}''_{O_2}(N) = \bar{\mu}'_{O_2}(Y) .$$

Hence equation (9) could be rewritten as

$$\begin{aligned} E_1 = -\frac{1}{F}[\int t_{Na^+}\mathrm{d}\bar{\mu}_{Na_2O}(N) + (t_{Na^+} - t_{O^{2-}})(\bar{\mu}''_{[O_2]} - \\ \bar{\mu}'_{[O_2]})(Y)] \end{aligned} \qquad (10)$$

Further, substituting equations $\bar{\mu}_i = \frac{\mu_i}{z_i}$ and $\mu_i = \mu_i^{\circ} + RT\ln a_i$ in equation (10), one get

$$E_1 = -t_{Na^+}\frac{RT}{2F}\ln\frac{a''_{Na_2O}}{a'_{Na_2O}}(N) + (t_{O^{2-}} - t_{Na^+})\frac{RT}{4F}\ln\frac{p''_{O_2}}{P'_{O_2}}(Y) \qquad (11)$$

where a'_{Na_2O} and a''_{Na_2O} are the activities of Na_2O at the left-hand and right-hand boundaries of phase NASICON respectively. p'_{O_2} and p''_{O_2} are oxygen partial pressures at the left-hand and right-hand boundaries of phase YSZ respectively. Equation (11) is the EMF equation of the new cell (7).

Secondly, one could calculate E_2 from Na_2CO_3 decomposition reaction. According to the change of Gibbs free energy of Na_2CO_3 decomposition reaction (8), $\Delta G_2 = \Delta G^\circ + RT\ln\frac{P_{CO_2}}{P^\ominus}$, and equation $\Delta G_2 = -nEF$, one get

$$E_2 = -\frac{\Delta G^\circ}{2F} - \frac{RT}{2F}\ln\frac{P_{CO_2}}{P^\ominus} .$$

Therefore the EMF equation of the cell (6) is

$$\begin{aligned} E = E_1 + E_2 = -\frac{\Delta G^\circ}{2F} - \frac{RT}{2F}\ln\frac{P_{CO_2}}{P^\ominus} - t_{Na^+}\frac{RT}{2F}\ln\frac{a''_{Na_2O}}{a'_{Na_2O}}(N) + \\ (t_{O^{2-}} - t_{Na^+})\frac{RT}{4F}\ln\frac{p''_{O_2}}{P'_{O_2}}(Y) \end{aligned} \qquad (12)$$

In addition, the activity of Na_2O (a'_{Na_2O}) is equal to 1 at the left-hand boundaries of NASICON, so equation (12) could be reduced to

$$\begin{aligned} E = -\frac{\Delta G^\circ}{2F} - \frac{RT}{2F}\ln\frac{P_{CO_2}}{P^\ominus} - t_{Na^+}\frac{RT}{2F}\ln a''_{Na_2O}(N) + \\ (t_{O^{2-}} - t_{Na^+})\frac{RT}{4F}\ln\frac{p''_{O_2}}{P'_{O_2}}(Y) \end{aligned} \qquad (13)$$

or

$$E = -\frac{\Delta G^{\circ}}{2F} - \frac{RT}{2F}\ln a_{\mathrm{Na_2O}}\frac{p_{\mathrm{CO_2}}}{p^{\ominus}} + t_e\frac{RT}{2F}\ln a_{\mathrm{Na_2O}} + (t_{\mathrm{O^{2-}}} - t_{\mathrm{Na^+}})\frac{RT}{4F}\ln\frac{p''_{\mathrm{O_2}}}{p'_{\mathrm{O_2}}}(\mathrm{Y}) \qquad (14)$$

where t_e is the electron transference number in phase NASICON.

5 Discussion

Supposed that there is no transportation of electrons in the double solid electrolyte or the transportation of electrons in the double solid electrolyte can be ignored, the transference numbers of Na^+ and O^{2-} are both equal to 1, and equation (14) can be reduced to equation (1).

Equation (1) could be considered as a special case of equation (14). Both equations have the same expression if the transports of electrons are ignored. However, owing to the transports of electrons, the transference number of Na^+ is not equal to the transference number of O^{2-}. In this situation, we have to take into account of the junction potential across the two electrolytes. Thus the term

$$t_e\frac{RT}{4F}\ln a_{\mathrm{Na_2O}} + (t_{\mathrm{O^{2-}}} - t_{\mathrm{Na^+}})\frac{RT}{4F}\ln\frac{p''_{\mathrm{O_2}}}{p'_{\mathrm{O_2}}}(\mathrm{Y})$$

in equation (14), which is the junction potential of the double solid electrolyte, must be included.

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