Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Non-Equilibrium Thermodynamics of Mixed Ionic-Electronic Conductive Electrodes and their Interfaces: A Ni/CGO Study

Nicholas J. Williams[1], Ieuan D. Seymour[1], Robert T. Leah[2], Aayan Banerjee[3], Subhasish Mukerjee[2] and Stephen J. Skinner[1*]

1. Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK
2. Ceres Power Ltd., Viking House, Foundry Lane, Horsham, RH13 5PX, UK
3. Catalytic Processes and Materials, Faculty of Science and Technology, University of Twente, Drienerlolaan 5, 7500 AE Enschede, the Netherlands

* s.skinner@imperial.ac.uk

Supplementary Information

Derivation of Eq. (6) and (7)

We begin with the general equation describing current density derived from transition state theory as the ratio between the rate of the forward and backward reactions:

$$j = ne\left(\overrightarrow{k}_0 e^{-\frac{(\mu_{TS}^{ex}-\mu_r)}{k_B T}} - \overleftarrow{k}_0 e^{-\frac{(\mu_{TS}^{ex}-\mu_p)}{k_B T}}\right) \tag{A 1}$$

The free energy of the transition state is given as:

$$\mu_{TS}^{ex} = \overset{\circ}{\mu}_{TS} + k_B T \ln \gamma_{TS} + (1-\beta)ne\phi_r + \beta ne\phi_p \tag{A 2}$$

By substituting (A 2) into the exponent of (A 1) yields the exponents:

$$\mu_{TS}^{ex} - \mu_r = \overset{\circ}{\mu}_{TS} - \overset{\circ}{\mu}_r + k_B T \ln \gamma_{TS} - k_B T \ln \prod_r (a_r)^{v_r} + \beta ne(\phi_p - \phi_r) \tag{A 3}$$

And

$$\mu_{TS}^{ex} - \mu_p = \overset{\circ}{\mu}_{TS} - \overset{\circ}{\mu}_p + k_B T \ln \gamma_{TS} - k_B T \ln \prod_p (a_p)^{v_p} + (1-\beta)ne(\phi_r - \phi_p) \tag{A 4}$$

where v_i is the stoichiometric coefficient of species i, a_i is the activity of species i, and the exponential term $\overset{\circ}{\mu}_i$ is the standard chemical potential of species i. (A 1) can then be expanded by removing the activity coefficient, activity and standard chemical potential terms from the exponential. We also assume that the attempt frequency for the forward and backward reactions are equivalent, such that $\overrightarrow{k}_0 = \overleftarrow{k}_0 = k_0$:[21]

$$j = \frac{nek_0}{\gamma_{TS}}\left(e^{\frac{(1-\beta)\mu_r^\circ+\beta\mu_p^\circ-\mu_{TS}^\circ}{k_BT}}\right)\left[\prod_r (a_r)^{v_r}\, e^{-\frac{\beta(-\mu_p^\circ+\mu_r^\circ+ne\phi_p-ne\phi_r)}{k_BT}} - \prod_p (a_p)^{v_p}\, e^{-\frac{(1-\beta)(-\mu_r^\circ+\mu_p^\circ+ne\phi_r-ne\phi_p)}{k_BT}}\right] \tag{A 5}$$

The equilibrium chemical potentials for the reactant and product states are given as:

$$\mu_r^{eq} = \mu_r^\circ + k_BT\ln\prod_r (a_r^{eq})^{v_r} + ne\phi_r^{eq} \tag{A 6}$$

$$\mu_r^{eq} = \mu_p^\circ + k_BT\ln\prod_p (a_p^{eq})^{v_p} + ne\phi_p^{eq} \tag{A 7}$$

At equilibrium $\mu_r^{eq} = \mu_r^{eq}$, expansion yields:

$$\mu_p^\circ - \mu_r^\circ = k_BT\ln\prod_r (a_r^{eq})^{v_r} - k_BT\ln\prod_p (a_p^{eq})^{v_p} + ne\left(\phi_r^{eq} - \phi_p^{eq}\right) \tag{A 8}$$

As such, the standard chemical potentials can be eliminated from inside the squared brackets of eq. (A 5):

$$j = \frac{nek_0}{\gamma_{TS}}\left(e^{\frac{(1-\beta)\mu_r^\circ+\beta\mu_p^\circ-\mu_{TS}^\circ}{k_BT}}\right)\left[\prod_r (a_r)^{v_r}\left(\frac{\prod_p (a_p^{eq})^{v_p}}{\prod_r (a_r)^{v_r}}\right)^{\beta} e^{-\frac{\beta ne(\Delta\phi_r-\Delta\phi_p)}{k_BT}} - \prod_p (a_p)^{v_p}\left(\frac{\prod_r (a_r^{eq})^{v_r}}{\prod_p (a_p)^{v_p}}\right)^{1-\beta} e^{-\frac{(1-\beta)ne(\Delta\phi_p-\Delta\phi_r))}{k_BT}}\right] \tag{A 9}$$

where we have made the simplification $\Delta\phi_i = \phi_i - \phi_i^{eq}$. Finally, (A 8) and (A 9) can be simplified as:

$$j = \frac{nek_0}{\gamma_{TS}}\left(\prod_r (a_r^{eq})^{v_r}\right)^{1-\beta}\left(\prod_p (a_p^{eq})^{v_p}\right)^{\beta}\left(e^{\frac{(1-\beta)\mu_r^\circ+\beta\mu_p^\circ-\mu_{TS}^\circ}{k_BT}}\right)\left[\prod_r\left(\frac{a_r}{a_r^{eq}}\right)^{v_r} e^{-\frac{\beta ne(\Delta\phi_r-\Delta\phi_p)}{k_BT}} - \prod_p\left(\frac{a_p}{a_p^{eq}}\right)^{v_p} e^{-\frac{(1-\beta)ne(\Delta\phi_p-\Delta\phi_r)}{k_BT}}\right] \tag{A 10}$$

The exchange current density is therefore given as:

$$j^0 = \frac{nek_0}{\gamma_{TS}}\left(\prod_r (a_r^{eq})^{v_r}\right)^{1-\beta}\left(\prod_p (a_p^{eq})^{v_p}\right)^{\beta} e^{\frac{(1-\beta)\mu_r^\circ+\beta\mu_p^\circ-\mu_{TS}^\circ}{k_BT}} \tag{A 11}$$

Thus, the current density is given as its standard form given in eq. (7):

$$\mathrm{j} = \mathrm{j}^0\left[\prod_{\mathrm{r}}\left(\frac{\mathrm{a_r}}{\mathrm{a_r^{eq}}}\right)^{\mathrm{v_r}} \mathrm{e}^{\frac{\beta \mathrm{ne}(\Delta\phi_\mathrm{r}-\Delta\phi_\mathrm{p})}{\mathrm{k_B T}}} - \prod_{\mathrm{p}}\left(\frac{\mathrm{a_p}}{\mathrm{a_p^{eq}}}\right)^{\mathrm{v_p}} \mathrm{e}^{\frac{-(1-\beta)\mathrm{ne}(\Delta\phi_\mathrm{r}-\Delta\phi_\mathrm{p})}{\mathrm{k_B T}}}\right] \tag{A 12}$$

Derivation of Eq. (11)

To derive Eq. (11) we begin with Eq. (10) which introduces the activation overpotential term:

$$\mathrm{e}\eta_{\mathrm{act}} = \Delta\mu_{\mathrm{Ce^x_{Ce}}} - \Delta\mu_{\mathrm{Ce'_{Ce}}} + \Delta\mu_{\mathrm{O^x_O}} - \Delta\mu_{\mathrm{OH^\bullet_O}} = \mathrm{k_B T}\ln\left(\frac{\mathrm{a^{eq}_{Ce'_{Ce}}}\,\mathrm{a^{eq}_{OH^\bullet_O}}}{\mathrm{a_{Ce'_{Ce}}}\,\mathrm{a_{OH^\bullet_O}}}\frac{\mathrm{a_{Ce^x_{Ce}}}\,\mathrm{a_{O^x_O}}}{\mathrm{a^{eq}_{Ce^x_{Ce}}}\,\mathrm{a^{eq}_{O^x_O}}}\right) + \mathrm{e}\Delta\chi_{\mathrm{OH^\bullet_O}} \tag{A 13}$$

With the knowledge that $\mathrm{R_2^{2PB}}$ is slow relative to all other reactions, we can state that $\mathrm{R_1^{2PB}}$ is in a state of quasi-equilibrium, such that:

$$\Delta\mu_{\mathrm{H_2O_{(g)}}} + \Delta\mu_{\mathrm{O^x_O}} + \Delta\mu_{\mathrm{V^{\bullet\bullet}_O}} = 2\Delta\mu_{\mathrm{OH^\bullet_O}} \tag{A 14}$$

(A 14) can be expanded as:

$$\mathrm{k_B T}\ln\left(\frac{\mathrm{a_{O^x_O}}\,\mathrm{a_{V^{\bullet\bullet}_O}}}{\mathrm{a^{eq}_{O^x_O}}\,\mathrm{a^{eq}_{V^{\bullet\bullet}_O}}}\right) + 2\mathrm{e}\Delta\phi_{\mathrm{CGO}} = 2\mathrm{k_B T}\ln\left(\frac{\mathrm{a_{OH^\bullet_O}}}{\mathrm{a^{eq}_{OH^\bullet_O}}}\right) + 2\mathrm{e}\Delta\phi_{\mathrm{OH^\bullet_O}} \tag{A 15}$$

where $\phi_{\mathrm{V^{\bullet\bullet}_O}} = \phi_{\mathrm{CGO}}$. The activity and electric potential terms can be separated:

$$2\mathrm{e}\Delta\phi_{\mathrm{CGO}} - 2\mathrm{e}\Delta\phi_{\mathrm{OH^\bullet_O}} = 2\mathrm{k_B T}\ln\left(\frac{\mathrm{a_{OH^\bullet_O}}}{\mathrm{a^{eq}_{OH^\bullet_O}}}\sqrt{\frac{\mathrm{a^{eq}_{O^x_O}}\,\mathrm{a^{eq}_{V^{\bullet\bullet}_O}}}{\mathrm{a_{O^x_O}}\,\mathrm{a_{V^{\bullet\bullet}_O}}}}\right) \tag{A 16}$$

Using eq. (9) we find an expression for the shift in electrostatic surface potential:

$$2\mathrm{e}\Delta\chi_{\mathrm{OH^\bullet_O}} = 2\mathrm{k_B T}\ln\left(\frac{\mathrm{a_{OH^\bullet_O}}}{\mathrm{a^{eq}_{OH^\bullet_O}}}\sqrt{\frac{\mathrm{a^{eq}_{O^x_O}}\,\mathrm{a^{eq}_{V^{\bullet\bullet}_O}}}{\mathrm{a_{O^x_O}}\,\mathrm{a_{V^{\bullet\bullet}_O}}}}\right) \tag{A 17}$$

Substituting (A 17) into (A 13) eliminates the electrostatic surface potential:

$$\mathrm{e}\eta_{\mathrm{act}} = \mathrm{k_B T}\ln\left(\frac{\mathrm{a^{eq}_{Ce'_{Ce}}}\,\mathrm{a^{eq}_{OH^\bullet_O}}}{\mathrm{a_{Ce'_{Ce}}}\,\mathrm{a_{OH^\bullet_O}}}\frac{\mathrm{a_{Ce^x_{Ce}}}\,\mathrm{a_{O^x_O}}}{\mathrm{a^{eq}_{Ce^x_{Ce}}}\,\mathrm{a^{eq}_{O^x_O}}}\right) + \mathrm{k_B T}\ln\left(\frac{\mathrm{a_{OH^\bullet_O}}}{\mathrm{a^{eq}_{OH^\bullet_O}}}\sqrt{\frac{\mathrm{a^{eq}_{O^x_O}}\,\mathrm{a^{eq}_{V^{\bullet\bullet}_O}}}{\mathrm{a_{O^x_O}}\,\mathrm{a_{V^{\bullet\bullet}_O}}}}\right) \tag{A 18}$$

(A 18) can be simplified to yield eq. (11):

$$\mathrm{e}\eta_{\mathrm{act}} = \mathrm{k_B T}\ln\left(\frac{\mathrm{a_{Ce^x_{Ce}}}}{\mathrm{a^{eq}_{Ce^x_{Ce}}}}\frac{\mathrm{a^{eq}_{Ce'_{Ce}}}}{\mathrm{a_{Ce'_{Ce}}}}\sqrt{\frac{\mathrm{a_{O^x_O}}}{\mathrm{a^{eq}_{O^x_O}}}\frac{\mathrm{a^{eq}_{V^{\bullet\bullet}_O}}}{\mathrm{a_{V^{\bullet\bullet}_O}}}}\right) \tag{A 19}$$

Derivation of Eq. (16)

Following eq. (7), the exchange current density j^0_{2PB} is given as a function of equilibrium activity of the products and reactants:

$$j^0_{2PB} = 2ek_0\left(a^{eq}_{Ce'_{Ce}}\, a^{eq}_{OH^{\bullet}_{O}}\right)^{2(1-\beta)}\left(a^{eq}_{Ce^{x}_{Ce}}\, a^{eq}_{O^{x}_{O}}\sqrt{a^{eq}_{H_{2,ads}}}\right)^{2\beta} \tag{A 20}$$

The equilibrium chemical potentials of R_2^{2PB} can be expressed as:

$$2\mu^{eq}_{Ce'_{Ce}} + 2\mu^{eq}_{OH^{\bullet}_{O}} = 2\mu^{eq}_{Ce^{x}_{Ce}} + 2\mu^{eq}_{O^{x}_{O}} + \mu^{eq}_{H_{2,ads}} \tag{A 21}$$

Upon expanding (A 21):

$$2\overset{\circ}{\mu}_{Ce'_{Ce}} + 2\overset{\circ}{\mu}_{OH^{\bullet}_{O}} - 2\overset{\circ}{\mu}_{Ce^{x}_{Ce}} - 2\overset{\circ}{\mu}_{O^{x}_{O}} - \overset{\circ}{\mu}_{H_{2,ads}} = k_B T \ln\left(\frac{a^{eq}_{Ce^{x}_{Ce}}\, a^{eq}_{O^{x}_{O}}\sqrt{a^{eq}_{H_{2,ads}}}}{a^{eq}_{Ce'_{Ce}}\, a^{eq}_{OH^{\bullet}_{O}}}\right) + 2e\chi^{eq}_{OH^{\bullet}_{O}} \tag{A 22}$$

Rearranging (A 22) gives the equilibrium activity of the products:

$$a^{eq}_{Ce'_{Ce}}\, a^{eq}_{OH^{\bullet}_{O}}\sqrt{a^{eq}_{H_{2,ads}}} = \left(a^{eq}_{Ce^{x}_{Ce}}\, a^{eq}_{O^{x}_{O}}\right) e^{\frac{-2(\Delta_r\mu^{\circ} + e\chi^{eq})}{k_B T}} \tag{A 23}$$

where $2\Delta_r\mu^{\circ} = 2\overset{\circ}{\mu}_{Ce^{x}_{Ce}} + 2\overset{\circ}{\mu}_{O^{x}_{O}} + \overset{\circ}{\mu}_{H_{2,ads}} - 2\overset{\circ}{\mu}_{Ce'_{Ce}} - 2\overset{\circ}{\mu}_{OH^{\bullet}_{O}}$ is the change in standard chemical potential between the initial and the final states. Substituting (A 23) into (A 20) introduces the electrostatic surface potential at equilibrium to the exchange current density:

$$j^0_{2PB} = 2ek_0\left(a^{eq}_{Ce'_{Ce}}\, a^{eq}_{OH^{\bullet}_{O}}\right)^2 e^{\frac{-\beta 2e(\Delta\mu^{\circ} + \chi^{eq})}{k_B T}} = 2ek_0^*\left(a^{eq}_{Ce'_{Ce}}\, a^{eq}_{OH^{\bullet}_{O}}\right)^2 e^{\frac{-2\beta e\chi^{eq}}{k_B T}} \tag{A 24}$$

where $k_0^* = k_0 e^{-(\overset{\circ}{\mu}_{TS} - \overset{\circ}{\mu}_{r})/k_B T}$.