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Supporting Information: Insight into the effect of configuration entropy of additives on the Seebeck coefficient

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Derivation of Eq. (1)

The Gibbs free energy on the hot side can be expressed as

$$G^{(\mathrm{H})} = N^{(\mathrm{H})}_{\mathrm{R}^{4-}}\mu^{(\mathrm{H})}_{\mathrm{R}^{4-}} + N^{(\mathrm{H})}_{\mathrm{O}^{3-}}\mu^{(\mathrm{H})}_{\mathrm{O}^{3-}} \tag{S1}$$

and that on the cold side can be expressed as

$$G^{(\mathrm{L})} = N^{(\mathrm{L})}_{\mathrm{R}^{4-}}\mu^{(\mathrm{L})}_{\mathrm{R}^{4-}} + N^{(\mathrm{L})}_{\mathrm{O}^{3-}}\mu^{(\mathrm{L})}_{\mathrm{O}^{3-}}, \tag{S2}$$

where N with the subscript and the superscript indicates the number of molecules in units of mol and μ with the subscript and the superscript indicates the chemical potential; H and L in the superscript indicate the high and the low temperatures, respectively (this notation is used for other quantities as well). R^{4-} and O^{3-} in the subscripts denote the components associated with these chemical species. Now, we introduce the extent of reaction denoted by ξ. The difference in the Gibbs free energy between the initial and the final states when the extent of reaction is ξ, is given by

$$\Delta G = G^{(\mathrm{f})} - G^{(\mathrm{i})} = \xi\mu^{(\mathrm{H})}_{\mathrm{O}^{3-}} - \xi\mu^{(\mathrm{H})}_{\mathrm{R}^{4-}} - \xi\mu^{(\mathrm{L})}_{\mathrm{O}^{3-}} + \xi\mu^{(\mathrm{L})}_{\mathrm{R}^{4-}}, \tag{S3}$$

where $G^{(\mathrm{i})} = G^{(\mathrm{H})} + G^{(\mathrm{L})}$ and $G^{(\mathrm{f})} = G^{(\mathrm{fH})} + G^{(\mathrm{fL})}$ with $G^{(\mathrm{fH})} = \left(N^{(\mathrm{H})}_{\mathrm{R}^{4-}} - \xi\right)\mu^{(\mathrm{H})}_{\mathrm{R}^{4-}} + \left(N^{(\mathrm{H})}_{\mathrm{O}^{3-}} + \xi\right)\mu^{(\mathrm{H})}_{\mathrm{O}^{3-}}$, and $G^{(\mathrm{fL})} = \left(N^{(\mathrm{L})}_{\mathrm{R}^{4-}} + \xi\right)\mu^{(\mathrm{L})}_{\mathrm{R}^{4-}} + \left(N^{(\mathrm{L})}_{\mathrm{O}^{3-}} - \xi\right)\mu^{(\mathrm{L})}_{\mathrm{O}^{3-}}$. The net electron charge of $-F\xi$, where $F = 9.6485 \times 10^4$ [C mol^{-1}] is the Faraday constant, is transferred by the extent of reaction, given by ξ. For $\mathrm{Fe(CN)_6}^{4-}/\mathrm{Fe(CN)_6}^{3-}$ redox reaction, $\mathrm{Fe(CN)_6}^{4-}$ transforms into $\mathrm{Fe(CN)_6}^{3-}$ on the hot side and $\mathrm{Fe(CN)_6}^{3-}$ transforms into $\mathrm{Fe(CN)_6}^{4-}$ on the cold side; electrons are transported from the hot side to the cold side. Using $\Delta V = V^{(\mathrm{H})} - V^{(\mathrm{L})}$, the work associated with electron transport can be expressed as $-F\xi\Delta V$. Owing to the energy conservation law associated with electron transport given by, $G^{(\mathrm{f})} = G^{(\mathrm{i})} - (-F\xi\Delta V)$, ΔV

can be expressed as $\Delta V = \Delta G/(F\xi)$; ΔV extracted from the system can be expressed as

$$\Delta V = \frac{-\Delta\mu^{(H)} + \Delta\mu^{(L)}}{F}, \tag{S4}$$

where $\Delta\mu^{(H)} = \mu^{(\mathrm{H})}_{\mathrm{R}^{4-}} - \mu^{(\mathrm{H})}_{\mathrm{O}^{3-}}$ and $\Delta\mu^{(L)} = \mu^{(\mathrm{L})}_{\mathrm{R}^{4-}} - \mu^{(\mathrm{L})}_{\mathrm{O}^{3-}}$.

Derivation of Eq. (16)

$w(\nu)$ is evaluated below. The rate of the increasing ν is proportional to the number of vacant sites $\nu_{\max} - \nu$ and $[\alpha]$, where $\nu_{\max}$ indicates the maximum number of coordinated molecules on R^{4-} or O^{3-}. The rate of the decreasing ν from the $\nu+1$ coordinated state is proportional to $\nu + 1$. The detailed balance in equilibrium given by

$$w(\nu+1)/w(\nu) = K_{\mathrm{eq}}[\alpha](\nu_{\max} - \nu)/(\nu+1) \tag{S5}$$

holds, where K_{eq} is the equilibrium constant. From $w(1)/w(0) = K_{\mathrm{eq}}[\alpha]\nu_{\max}$ and $w(2)/w(1) = K_{\mathrm{eq}}[\alpha](\nu_{\max} - 1)/2$, $w(2)/w(0) = K^2_{\mathrm{eq}}[\alpha]^2\nu_{\max}(\nu_{\max} - 1)/2$ is obtained. In general,

$$w(\nu)/w(0) = K^{\nu}_{\mathrm{eq}}[\alpha]^{\nu}\,{}_{\nu_{\max}}C_{\nu}, \tag{S6}$$

where ${}_{\nu_{\max}}C_{\nu}$ is defined as ${}_{\nu_{\max}}C_{\nu} = \nu_{\max}!/[(\nu_{\max} - \nu)!\nu!]$. From the normalization condition given by $\sum_0^{\nu_{\max}} w(\nu) = 1$,

$$w(0) = 1/(\sum_0^{\nu_{\max}} K^{\nu}_{\mathrm{eq}}[\alpha]^{\nu}\,{}_{\nu_{\max}}C_{\nu}) \tag{S7}$$

$$= 1/(1 + K_{\mathrm{eq}}[\alpha])^{\nu_{\max}} \tag{S8}$$

is obtained. Lastly,

$$w(\nu) = K_{\mathrm{eq}}^{\nu}[\alpha]^{\nu}{}_{\nu_{\max}}C_{\nu}/(1+K_{\mathrm{eq}}[\alpha])^{\nu_{\max}}. \tag{S9}$$

By considering that K_{eq} in the high-temperature region is denoted by $K_{\mathrm{eq}}^{(H)}$, $w(\nu)$ is obtained as

$$w(\nu) = \frac{K_{\mathrm{eq}}^{(H)\nu}[\alpha]^{\nu}{}_{\nu_{\max}}C_{\nu}}{(1+K_{\mathrm{eq}}^{(H)}[\alpha])^{\nu_{\max}}}. \tag{S10}$$

We also prove $\sum_{\nu=0}^{\nu_{\max}} w(\nu)\nu = \nu_{\max}[\alpha]K_{\mathrm{eq}}^{(H)}/\left[1+[\alpha]K_{\mathrm{eq}}^{(H)}\right]$.

Firstly,

$$\sum_{0}^{\nu_{\max}} \nu r^{\nu}{}_{\nu_{\max}}C_{\nu} = r\frac{\partial}{\partial r}\sum_{1}^{\nu_{\max}} r^{\nu}{}_{\nu_{\max}}C_{\nu}, \tag{S11}$$

$$= r\frac{\partial}{\partial r}(1+r)^{\nu_{\max}} \tag{S12}$$

$$= \nu_{\max} r(1+r)^{\nu_{\max}-1}, \tag{S13}$$

is calculated and $r = K_{\mathrm{eq}}[\alpha]$ is introduced. Subsequently,

$$\sum_{0}^{\nu_{\max}} \nu w(\nu) = \frac{\nu_{\max}K_{\mathrm{eq}}[\alpha]}{1+K_{\mathrm{eq}}[\alpha]} \tag{S14}$$

is obtained.