# GRAHAME EQUATION GENERALIZED TO STUDY IONIC THERMOELECTRIC SUPERCAPACITORS

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## ABSTRACT

Recently, ionic thermoelectric supercapacitors have gained attention owing to its high electromotive force (EMF) of 10 mV/K. In ionic thermoelectric supercapacitors, the high EMF has been achieved using redox-inactive ions in an open circuit condition. Herein, we theoretically estimated EMF generated in the Stern layer, and the diffuse layer by taking into account the temperature gradient and the Eastman entropy of transfer. The EMF is obtained by solving self-consistent equations using the adsorption isotherm as schematically shown in Fig. 1. The Grahame equation has been generalized to consider the parts in the dotted line in Fig. 1.

The current density of cations ($j_+$) can be expressed using the cation concentration($n_+$), diffusion constant of cations ($D_+$), electric field ($E$), the valency of cations ($z$) and the elementary charge ($q$) as

$$j_+ = -D_+ \left( \frac{\partial}{\partial x} n_+ - \frac{z_+ q E n_+}{k_B T} + \frac{\hat{S}_+}{k_B T} n_+ \frac{\partial}{\partial x} T \right), \tag{1}$$

where $\hat{S}_+ = \alpha_+ k_B$ indicates the Eastman entropy of transfer and $\alpha_+$ is the dimensionless Eastman entropy of transfer. Using $E(x) = -\partial\psi(x)/(\partial x)$, Eq. (1) can be integrated. As the boundary condition, we consider the surface charge density ($\sigma$).

The generalized Grahame equation is obtained as

$$\left| \frac{z_+ q \Psi_i}{k_B T_i} - \frac{z_+ q \psi_m}{k_B T_m} \right| \approx \cosh^{-1} \left[ \left( \frac{T_i}{T_m} \right)^{\alpha - 1} \left( 1 + \frac{\sigma^2}{4 \varepsilon_r \varepsilon_0 n_m k_B T_m} \right) \right], \tag{2}$$

where $\varepsilon_r$ and $\varepsilon_0$ are the relative and vacuum dielectric constant of electrolyte, respectively; we used $\cosh^{-1}(x) = \ln(x + \sqrt{x^2 - 1})$ if $x \geq 0$. The quantities with the subscript i are those at the closest distance to the electrode. The quantities with the subscript m are those at distances away from the electrode so that the charge neutrality can be assumed in the electrolyte. The EMF of $2-3$ mV/K is estimated after solving the self-consistent equations.

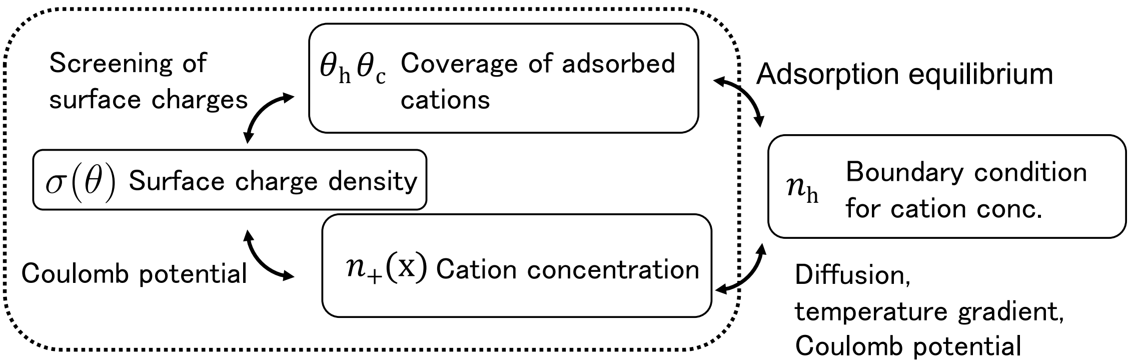


Figure 1: Theoretical formulation of thermoelectric supercapacitors: Grahame equation is generalized for the parts in the dotted line.

Keywords: Seebeck coefficient, Grahame equation, Eastman entropy of transfer

Physics and Astronomy Classification Scheme: 82.60.Lf,73.50.Lw

## REFERENCES

[1] S. Horike, V. Nandal, Q. Wei, and K. Seki, Contributions of Both the Eastman Entropy of Transfer and Electric Double Layer to the Electromotive Force of Ionic Thermoelectric Supercapacitors, ACS Appl. Mater. Interfaces, 17, (2025), 4984–4995 .