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On the time-dependent electrolyte Seebeck effect

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ABSTRACT

Single-ion Soret coefficients α_i characterize the tendency of ions in an electrolyte solution to move in a thermal gradient. When these coefficients differ between cations and anions, an electric field can be generated. For this so-called electrolyte Seebeck effect to occur, different thermodiffusive fluxes need to be blocked by boundaries—electrodes, for example. Local charge neutrality is then broken in the Debye-length vicinity of the electrodes. Confusingly, many authors point to these regions as the source of the thermoelectric field yet ignore them in derivations of the time-dependent Seebeck coefficient $S(t)$, giving a false impression that the electrolyte Seebeck effect is purely a bulk phenomenon. Without enforcing local electroneutrality, we derive $S(t)$ generated by a binary electrolyte with arbitrary ionic valencies subject to a time-dependent thermal gradient. Next, we experimentally measure $S(t)$ for five acids, bases, and salts near titanium electrodes. For the steady state, we find $S \approx 2$ mV K^{-1} for many electrolytes, roughly one order of magnitude larger than the predictions based on literature α_i. We fit our expression for $S(t)$ to the experimental data, treating the α_i as fit parameters, and also find larger-than-literature values, accordingly.

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