

Orientation effects in hydrodynamic instability in concentration polarization

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One dimensional steady state passage of the electric current from an aqueous electrolyte solution into a charge selective (perm-selective) solid, such as a metal electrode or ion exchange membrane, is hydro-dynamically unstable, [1]-[3]. For a long time this instability has been attributed to electro-convection related to the extended space charge which forms at the outer edge of the electric double layer at the limiting current, [4]-[10]. For the perfectly perm-selective solid with infinite conductivity this mechanism is the only possible one. Recently, it has been shown that for a non-perfectly perm-selective membrane, or for a perfectly perm-selective membrane with finite conductivity (commercial ion-exchange membranes are practically perfectly perm-selective), additional electro-convective instability mechanisms non-related to the extended space charge are possible, [11]-[13].

All of the aforementioned studies focused on electro-convective instability mechanisms because it was recognized the gravitational mechanism could not yield instability for most practical situations (sub-millimeter electrolyte systems with concentration below one centimolar and without a forced stirring). In such systems, the passage of electric current results in formation of concentration variations near the perm-selective solid known as concentration polarization (CP). The expression of CP is a characteristic voltage current dependence with a current saturation at the limiting value (limiting current, corresponding to a nearly vanishing interface electrolyte concentration) followed by a current increase with voltage known as the over-limiting conductance regime. For some systems, transition to the over-limiting conductance is accompanied by the appearance of excessive electric noise. Commonly, over-limiting conductance sets on due to the mechanical stirring of the interface diffusion layer resulting from a hydrodynamic electroconvective instability of quiescent electric conduction. In relation to possible gravitational mechanisms, the CP-induced density stratification results both from direct concentration variation and its related non-uniform Joule heating. The temperature variations related to the latter usually do not exceed one degree Kelvin. As a result, for gravitationally unstable orientation with the depleted interface at the bottom, the Rayleigh number related to the thermally induced density stratification is usually smaller than that related to concentration variation, whereas the latter is lower than the Rayleigh-Benard instability threshold. For this reason, electro-convective mechanisms have been invoked to explain the instability, and no systematic study of the Joule heating effects in CP has been undertaken until recently (not long ago, the effect of density stratification related to concentration variation upon the electroconvective instability in CP has been addressed in Ref. [14]).

Lately, this shortcoming has been remedied in the theoretical studies by Demekhin and his group, [15]. They discovered a very interesting possibility of a Joule heating related instability

expected to occur for overall stable density stratification (depleted interface on the top). In this presentation we investigate this possibility both experimentally and theoretically.

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