

Экспресс-метод измерения параметров кроссовера для галогенатных источников тока

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Express method to measure crossover parameters for halogenate power sources

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Ion-exchange membrane are widely used as separators of various types of chemical power sources, in particular redox flow batteries (RFB). Their principal characteristics for such applications are related to crossover of components between half-cells which are determined both by the distribution constants of these species at the membrane/solution boundary, K , and by their transport rate inside membrane, D .

Traditional procedures based on their transmembrane transfer between two compartments (H-cells) require long-term experiments.

A faster approach is based on measurements of the flux of a gas or solute electroactive component through membrane from its feed space towards a porous or mesh electrode pressed to its surface where it reacts under transport-limited conditions. The electrode is polarized owing to counter and reference electrodes located inside the same compartment filled in electrolyte solution so that transmembrane transport takes place without imposed electric field inside membrane. Rapid addition of the reacting component into the feed camera leads to a non-stationary current; its registration allows one to determine its K and D values. This method requires to use specially arranged laboratory equipment.

In some other studies the electrode surface is covered by a thin membrane layer (e.g. of Nafion) deposited from a corresponding precursor solution. Such modified electrode can be immersed into solution of the component under consideration, with subsequent registration of steady-state or non-stationary current. Each measurement needs generally to prepare a new film-coated electrode.

We have proposed to determine the crossover parameters, K and D , of any electroactive species from measurements of its non-stationary discharge current at disk electrode through an ion-exchange membrane which is pressed mechanically to the electrode surface while the external membrane surface is in contact with solution containing dissolved species. Unlike the above quoted studies the membrane space is filled with species from solution up to its equilibrium concentration prior to the potential step to the value ensured the non-stationary diffusion-limited transport of species from solution towards electrode surface through membrane. After the steady-state current has been achieved the electrode potential may be changed in stepwise manner in order to induce the backward transformation of the product of the former redox reaction.

Theoretical analysis has provided us with analytical expressions for the current variation

which may be used to determine both the distribution constant of the initial species and the diffusion coefficients of the species and of its reaction product.

Feasibility of the proposed method has been demonstrated on the transmembrane (Nafion) transport of halide ions, X^- ($X = \text{Br}$ or Cl) induced by their electroreduction at electrode surface into the corresponding halogen molecules, X_2 , followed by the backward electrooxidation of X_2 molecules to X^- anions. Treatment of these experimental data for non-stationary current has given such crossover parameters: $K(X^-)$, $D(X^-)$ and $D(X_2)$ for various external aqueous solutions containing H_2SO_4 and additions of HX or NaX .