

**SOLID ELECTROLYTE INTERPHASE (SEI) ELECTRODES
PART VII. THE ELECTROCHEMICAL BEHAVIOUR OF CALCIUM IN
Ba(AlCl₄)₂ AND Sr(AlCl₄)₂-THIONYL CHLORIDE SOLUTIONS
(EXTENDED ABSTRACT)**

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The Ca-thionyl chloride (TC) cell is an SEI battery [1] in which the calcium anode is covered by a solid electrolyte film. The corrosion of calcium in CaX₂ (X = AlCl₄)-TC solutions is too high, and so this electrolyte is not suitable for most practical applications. This high rate of corrosion results from the fact that the CaCl₂ SEI does not provide the anode with sufficient corrosion protection. There are several possible reasons for this fast self-discharge. Two reasons which appear to be the most important are [2, 3]: (a) too-high a solubility of CaCl₂ in the electrolyte; (b) a combination of a high anionic transference number ($t_- \sim 1$) and a large difference between the equivalent volume of CaCl₂ (V_{mx}) and that of calcium (V_m).

During the corrosion process and, of course, during the discharge process Cl⁻ ions travel through the SEI from the solution interface to the metal interface, where CaCl₂ is formed. The formation of CaCl₂, whose volume is twice that of calcium, generates stresses in the CaCl₂ film. This can lead to crack formation if the film is not sufficiently elastic.

The goal of this work was to try to change the chemical composition and the properties of the SEI by a partial or total replacement of the calcium cation by strontium or barium. This was done by replacing CaX₂ by SrX₂ or BaX₂.

The corrosion rate of 0.5 mm calcium foil (99.9% Pfizer) in 1 M SrX₂ and 1 M BaX₂ was measured at 70 °C from the weight loss of calcium strips stored in sealed glass ampules, and at 20 °C using an LKB model 2277 micro-calorimeter. The resistance, apparent thickness, and resistivity of the SEI were determined by a.c. measurements. The morphology and the chemical composition of the protective film were determined using a scanning electron microscope.

The weight loss of calcium after 4 weeks storage in 1 M BaX₂ and in 1 M SrX₂ was 8% and 10%, respectively, by comparison with a weight loss of 24% in 1 M CaX₂. In addition, the corrosion in SrX₂ and BaX₂ solutions is free from pits and much more homogeneous than in CaX₂ solutions. The

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heat output of calcium immersed in 1 M BaX_2 or 1 M SrX_2 at 20 °C is about 10% - 20% of that immersed in 1 M CaX_2 . C-size hermetically sealed cells containing 0.7 M SrX_2 did not lose capacity after four weeks of storage at 70 °C [2, 3].

The chemical composition of the protective film formed in 0.7 - 1 M BaX_2 solutions is 96+% CaCl_2 and 1 - 4% BaCl_2 . This film seems to be more compact and more amorphous than the CaCl_2 film formed in CaX_2 solutions. The film formed in 0.7 - 1 M SrX_2 consists mainly of SrCl_2 and has needle-like crystals. The Sr:Ca ratio in the film is 2:1 after 70 days of storage in 1 M SrX_2 at room temperature, and 4:1 after four weeks of storage at 70 °C.

The a.c. spectra for the Ca SEI electrode were measured using hermetically sealed three-electrode cells. A typical spectrum for this electrode in 0.7 M SrX_2 has a spiral form (Fig. 1). The upper (positive) arc has a somewhat depressed shape and sometimes seems to be a combination of two nearby arcs. During storage in SrX_2 -TC solutions, R1 and R2 (Fig. 1) increase. The upper arc approaches a perfect semi-circle (less depressed) and the peak of the upper arc shifts to lower frequencies. The ratio R1/R2 decreases with time from about 5 after the first day, to about 1.5 after one month of storage. The resistivity of the SEI increases from 10^{10} to 10^{11} cm during one month of storage, while the apparent thickness stays about the same 20 - 50 Å. The corrosion mechanism of calcium in this system suggests that the inner part of the SEI, near to the Ca/SE interface, consists of CaCl_2 , while the outer part of the SEI near to the SE/solution interface, consists mostly of SrCl_2 . This outer SrCl_2 layer is formed by the exchange of Ca^{2+} cations in the CaCl_2 SEI with Sr^{2+} cations in the solution, indicating that

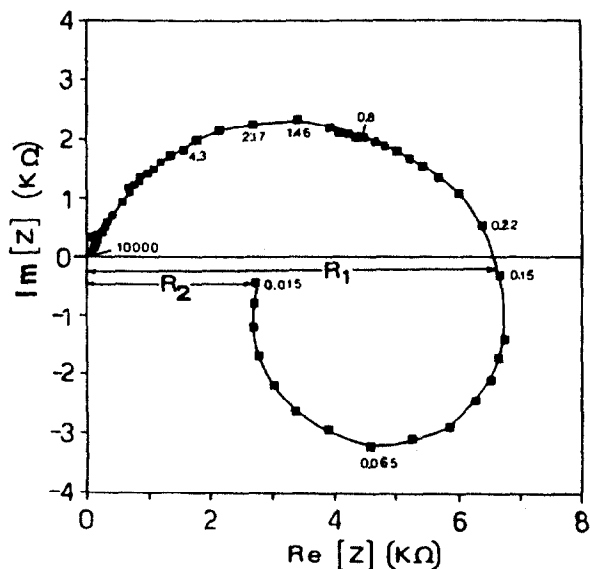


Fig. 1. An a.c. spectrum for a calcium electrode in 0.75 M SrX_2 solution after 45 days of storage at RT. Ca electrode in $\text{Sr}(\text{AlCl}_4)_2$. Area: 7 cm²; conc.: 0.7 M.

SrCl_2 is less soluble in this electrolyte. The changes in the a.c. spectra and in the resistivity of the SEI reflects this type of process. It indicates that the resistivity of SrCl_2 is somewhat higher than that of CaCl_2 . The lower arc was measured in CaX_2 , SrX_2 and BaX_2 -TC solutions, but not in LiX -TC solutions [4]. There may be several reasons for its existence, but it seems that the predominant one is the mix-type conductions in the MCl_2 -SEI i.e., t_+ and $t_- > 0$. This kind of interpretation has been suggested for the passivation of metals in aqueous solutions [5]. The a.c. spectra of the Ca electrode in BaX_2 solutions, and its time dependence are similar to that described above. The apparent thickness and resistivity of the SEI are also similar.

References

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