Complexing of Al\textsuperscript{3+} by S\textsuperscript{2–} Ions in Alkali Halide Melts

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nonstoichiometry will improve the electrocatalytic behavior of RuO₂ films. Unlike normal semiconductor films, those of RuO₂ are generally highly conducting; the main resistance component is probably due to intergranular contact resistance in these microcrystalline layers.

The main point of Dr. Burke's remarks, as we understand it, is that there are no reasons to expect that the electrocatalytic activity of RuO₂ electrodes should be influenced by nonstoichiometry since the active surface sites at high anodic potentials are invariably Ru(VI) species. While we do not feel like agreeing on this concept in principle, we contend that Dr. Burke's criticism is not properly addressed. Figure 1 on p. 1890 and the related comment in our paper clearly point out that "cracked" and "compact" electrodes differ in the surface morphology rather than in the nonstoichiometry. Figure 3 shows that no appreciable difference is observed within each group of electrodes although the nonstoichiometry varies largely, yet a difference possibly exists between the two groups, which may, thus, be related to the surface morphology. Therefore, the meaning of this paper is that morphology rather than nonstoichiometry is the crucial factor in electrocatalysis at RuO₂ anodes.

That the surface morphology can affect the electrocatalytic properties of RuO₂ has been shown in our previous work on O₂ evolution on some sets of electrodes. The effect is in fact more striking, and our conclusions have been confirmed in different laboratories. It has been neatly found that the degree of crystallinity has a definite effect on the O₂ evolution mechanism. The point of zero charge of RuO₂ samples has been found, to depend on the temperature of preparation and to be related, as expected, to the surface morphology, with the crystal parameters of the powder.

All of these observations emphasize the extreme sensitivity of the nature of the active sites to the morphology of the surface. Dr. Burke contends that the degree of hydration is not expected to be important in imparting the electrocatalytic properties. It is well established, however, that a number of properties of RuO₂ are closely interrelated as a function of the temperature of preparation. Thus, the residual hydration decreases as T increases and at the same time the crystallinity increases. Hydration is presumably located in grain boundaries or at "inner" surfaces (pores, etc.). As the crystallites grow, RuO₂ grow, defect-rich regions will shrink. That is what Fig. 9 in our paper is devised to point out.

In Dr. Burke's opinion, we have not paid much attention to the above aspect apparently because we have not appreciated some points he touches upon in his comments. (i) Reversibility of the Cl₂ reaction: This is easily proved by the fact that we were able to measure the exchange current from equilibrium I-E curves if not footnotes. The effect of main transfer on the Tafel slope has been discussed by one of us in a previous paper precisely in connection with the Cl₂ evolution reaction. We think that Losev's results highlight this aspect at the best. We have also suggested that Losev's idea could account for the results in Fig. 3 but that we cannot offer any definite proof for this. In a chapter written by two of us, the contrast between O₂ evolution as a "demanding," irreversible reaction and Cl₂ evolution as a reversible, possibly "facile" process has been exhaustively discussed. (ii) Relevance of surface redox behavior: We first suggested that the behavior of RuO₂ electrodes should be accounted for in terms of surface redox couples. The involvement of surface redox couples in electrocatalytic reactions has been recently rationalized by Krish- talked.

In any case, it is hard to think that the surface redox behavior is substantially unaffected by the solid phase composition. While the growth of a surface layer of more oxidized species might offset some of the expected differences, the features of the overlayer are still expected to depend on the characteristics of the underlying layer. Oxidized oxygen evolution may lead to a composition profile in the overlayer which might smooth down initial differences between differently treated samples. However, in the case of Cl₂ evolution, the large specific adsorption of CI- is to be taken into account when envisaging surface oxidation mechanisms. It is possible that some of the experiments cited by Burke are not sensitive enough to give evidence to surface effects. The free energy of a crystal is certainly affected by nonstoichiometry, and this is expected to be the case also for the surface where additional factors (morphology) have however to be taken into consideration. (iii) Nonstoichiometry and conductivity: Dr. Burke contends that, unlike semiconducting oxides, RuO₂ conduction properties are not affected by nonstoichiometry since it is a metallic conductor. Therefore, no improvement in the electrocatalytic properties are to be expected from this point of view. We certainly did not expect any effect of this sort since we drew attention to the metallic features of RuO₂ early in our work. Dr. Burke's statement (with no reference) that the main resistance component in RuO₂ films is probably due to intergranular contact resistance has been experimentally substantiated in this laboratory and shown in a paper where the main goal has been to emphasize the role of morphology in imparting "apparent semiconducting properties" towards RuO₂ films or pressed powders.
band has been repeatedly interpreted as the characteristic strong ν3 fundamental mode of vibration of the \([\text{AlCl}_4]^{-}\) tetrahedron. The solids [M\(\text{AlCl}_4\)] with M = Li, Na, K, etc. definitely contain tetrahedral \([\text{AlCl}_4]^{-}\) ions (according to several definitive single crystal x-ray structure solutions,\(^{29}\)) and they also give the same ν3 Raman band.\(^{29}\) In this way, there can be no doubt that \(\text{Al}^{3+}\) predominately exists as \([\text{AlCl}_4]^{-}\) ions in LiCl-KCl melts. The point has been neglected by the authors of the note; they merely mention as a possibility that the bonding between \(\text{Al}^{3+}\) and Cl\(^-\) cannot be wholly ionic.

Secondly, regarding mixed solutions of \(\text{AlCl}_3\) and Li\(_2\)S in pure chloride melts such as LiCl-KCl or LiCl-CsCl eutectics, the situation is the same though not as clear-cut. Our Raman spectroscopic and other evidence\(^{30}\) indicates the formation of polymeric species such as \([\text{Al}_n\text{S}_m\text{Cl}_{2m-2n}]^{-}\) with \(n \geq 3\). We are sure, as are the authors of the note, that new complex species are indeed formed upon the addition of sulfides to the solutions of \(\text{AlCl}_3\) in chloride melts; new Raman bands appear due to these new species (most notably near 325 cm\(^{-1}\)).\(^{30}\) But, contrary to the authors of the note, we find no reason to postulate species devoid of chlorine, such as \([\text{Al}_n\text{S}_m\text{C}_{2m-2n}]^{-}\). Rather, we have presented evidence that the mixed solution contains \([\text{Al}_n\text{S}_m\text{Cl}_{2n-2m}]^{-}\) (e.g. the presence of a pure polymeric compound \(\text{CsAlCl}_4\) with a similar Raman spectrum).\(^{30}\)

The so-called “4C model,” like other similar pure electrolyte models in physical chemistry, is simple and easy to use in calculations, but the results are of little or no value as long as chemical bonds are involved. The Raman evidence shows that the case in this considered system is therefore the predictions obtained by the “4C model” are of little if any use. This conclusion takes nothing from the value of the experimental results obtained by the authors.

Z. Nagy, J. L. Settle, J. Padova, and M. Blander: The comments by Berg and Bjerrum are based on a misunderstanding of our use of the concept of complexing which may not have been clearly stated in our paper. We will attempt to clarify our view of this concept in this reply.

In binary systems of any two chlorides, the nearest neighbors of all cations are almost exclusively chloride ions, and all cations are, in a sense, complexed by anions. Thus, the difference between the “complexing” of Li\(^+\), \(\text{Al}^{3+}\), or even K\(^+\) in binary LiF-KF melts (LiCl-KCl, LiCl-CsCl, etc.) is one of degree not of kind. It is, of course, proper to define special complexes such as \(\text{AlCl}_4^{-}\) in alkali halide melts where there is strong spectroscopic evidence for the existence of this species and where we believe the \(\text{AlCl}_4^{-}\) is likely to be the major, if not exclusive, \(\text{Al}^{3+}\) containing species. Whether these complexes exist depends on unknown factors related to the relative sensitivity of detecting these other species. Because there is always some uncertainty about the distribution of species (e.g., there could be some \(\text{Al}^{3+}\) ions with coordination other than 4), it is more exact and safer to avoid defining the species in work such as is described in our paper. (This is even more important in other systems where the coordination species are more poorly understood or defined than in melts dilute in \(\text{Al}^{3+}\).)

Contrary to Berg and Bjerrum’s comment, we did not assume that \(\text{Al}^{3+}\) and Cl\(^-\) are not part of a complex nor that the \(\text{AlCl}_4^{-}\) species does not exist. Thus, their second paragraph restates, but does not understand, our paper and is not on point of contention. For the purposes of our paper, the definition of such species (\(\text{AlCl}_4^{-}\)) was irrelevant and unnecessary. The \(\text{Al}^{3+}\) ions have some average nearest neighbor environment and could be exclusively four coordinated or could have some distribution of coordination numbers. The Cl\(^-\) ion will also have some average environment which or could have some distribution of coordination numbers.

References therein.


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\(^{33}\) See e.g. F. Wallart, A. Lorriaux-Rubbens, M. Gaierose, P. Barbier, and J. P. Wignacourt, J. Raman Spectrosc., 9, 55 (1980) and references therein.

\(^{34}\) L. A. Curtiss, Personal communication.


\(^{36}\) N. A. Curtiss, Personal communication.