Complexing of Al⁺³ by S⁻² Ions in Alkali Halide Melts

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nonstoichiometry will improve the electrocatalytic behavior of RuO$_2$ films. Unlike normal semiconductor films, those of RuO$_2$ are generally highly conducting; the main resistance component is probably due to intergranular contact resistance in these microcrystalline layers.

S. Ardizzone, A. Carugati, G. Lodi, and S. Trasatti

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 RuO$_2$ 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. 1690 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 mechanism from this paper is that morphology rather than nonstoichiometry is the crucial factor in electrocatalysis at RuO$_2$ anodes.

That the surface morphology can affect the electrocatalytic properties of RuO$_2$ has been shown in our previous work on O$_2$ evolution on some sets of electrodes. The effect of the temperature of preparation and to be related, as experiments have been confirmed in different laboratories. It has been neatly found that the degree of crystallinity has a definite effect on the O$_2$ evolution mechanism. The point of zero charge of RuO$_2$ samples has been found to depend on the temperature of preparation and to be related, as expected, to the temperature of preparation, with the crystal parameters of the electrode. 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 RuO$_2$ 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 (poles, etc.). As the crystallinity of RuO$_2$ grow, defect-rich regions will shrink.

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 Cl$_2$ reaction: This is easily proved by the fact that we were able to measure the exchange current from equilibrium i-E curves [cf. footnote 23]. The effect of mass transfer on the Tafel slope has been discussed by one from equilibrium i-E curves [cf. footnote 23]. The effect of nonstoichiometry varies largely, yet a difference possibly exists between the two groups, which may, thus, be related to the surface morphology. Therefore, the mechanism from this paper is that morphology rather than nonstoichiometry is the crucial factor in electrocatalysis at RuO$_2$ anodes.

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(ii) Relevance of surface redox behavior: We first suggested that the behavior of RuO$_2$ 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- after the 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 mechanism from this paper is that morphology rather than nonstoichiometry is the crucial factor in electrocatalysis at RuO$_2$ anodes.

(ii) Relevance of surface redox behavior: We first suggested that the behavior of RuO$_2$ 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- talk. 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. Longed 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 Cl$_2$ evolution, the large specific adsorption of Cl$_2$ 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 consider-ation. (iii) Nonstoichiometry and conductivity: Dr. Burke contends that, unlike semiconducting oxides, RuO$_2$ con-duction 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 RuO$_2$ early in our work. Dr. Burke’s statement (with no reference) that the main resistance component in RuO$_2$ 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 again to emphasize the role of morphology in imparting “appar-ent semiconductor properties” to RuO$_2$ films or pressed powders.

Complexing of Al$^{13}$ by 5–1 Ions in Alkali Halide Melts

Z. Nagy, J. L. Settle, J. Padova, and M. Blander

We would like to raise some general criticism regarding the interpretation of these new results in the light of our work, especially in relation to the proposed (and questionable) so-called “charge compensated coulomb complex” or “4C” model.

First, consider the question of the degree of complexation between Al$^{13}$ and Cl$^-$ in sulfide-free chloride melts, either be it LiCl-KCl or LiCl-CsCl. Apparently, the authors of the note in their “4C” model treat the A1$^{3+}$ and C1$^-$ as essen-tially uncomplexed. This is not in agreement with present common accepted knowledge, according to which [AlCl$_4$]$^{-}$ complex ions should be formed under such conditions.

We are sure that this formation of [AlCl$_4$]$^{-}$ takes place, because the Raman spectra of AlCl$_3$ dissolved in pure chloride melts show a strong polarized band at ca. 347 cm$^{-1}$. This 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 consider-ation. (iii) Nonstoichiometry and conductivity: Dr. Burke contends that, unlike semiconducting oxides, RuO$_2$ con-duction 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 RuO$_2$ early in our work. Dr. Burke’s statement (with no reference) that the main resistance component in RuO$_2$ 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 again to emphasize the role of morphology in imparting “appar-ent semiconductor properties” to RuO$_2$ films or pressed powders.

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band has been repeatedly interpreted as the characteristic strong ν, fundamental mode of vibration of the \([\text{AlCl}_4]^-\) tetrahedron. The solids \([\text{MAlCl}_3]\) with \(\text{M} = \text{Li, Na, K}\), 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 \(\nu\), Raman band.\(^{29}\) In this way, there can be no doubt that \(\text{Al}^{3+}\) predominantly 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 \(\text{Cl}^-\) could be not totally ionic.

Secondly, regarding mixed solutions of \(\text{AlCl}_3\) and \(\text{Li}_2\text{S}\) 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\(^{32}\) indicates the formation of polymeric species such as \([\text{Al}_n\text{S}_x\text{Cl}_{2n-x}]^-\) with \(n \geq 3\). We are sure, as are the authors of the note, that these new 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\(^{-1}\)).\(^{32}\) But, contrary to the authors of the note, we find no reason to postulate species devoid of chlorine, such as \([\text{Al}_n\text{S}_x\text{Cl}_{2n-x}]^-\). Rather, we have presented evidence that the mixed solution contains \([\text{Al}_n\text{S}_x\text{Cl}_{2n-x}]^-\) (e.g., the presence of a pure polymeric compound \(\text{CsAlCl}_4\) with a similar Raman spectrum).\(^{33}\)

The so-called “4C” model, like other similar purely electrostatic 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 these considered systems 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:\(^{40}\)

The comments by Berg and Bjerrum are based on a misunderstanding of our use of the concept of complexing which may have been clearly stated in our paper. We 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 \(\text{Li}^+\), \(\text{Al}^{3+}\), or even \(\text{K}^+\) cations in a solution of LiCl-KCl, and that of \(\text{Al}^{3+}\) 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 species 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 \(\text{Cl}^-\) are not part of a complex nor that the \([\text{AlCl}_4]^-\) species does not exist. Thus, their second paragraph rests on a misunderstanding of our paper and is not in point of contention. For the purposes of our paper, the definition of such species ([AlCl\(_4\)])\(^{-}\) is 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 \(\text{S}^-\) ion will also have some average environment which need not be specified. When the \(\text{Al}^{14+}\) and \(\text{S}^-\) ions associate, one can break down the process into two changes. The first is the replacement of a \(\text{Cl}^-\) in the first shell of an \(\text{Al}^{14+}\) by \(\text{S}^-\) and the replacement of an alkali ion in the first shell of the \(\text{S}^-\) by an \(\text{Al}^{14+}\) leading to a net energy change of about \(-2e^2/d\). The second change is the rearrangement of the other neighboring alkali and halide ions which is related to the optimization of the geometry of this intermediate. Berg and Bjerrum make the unsupported claim that bonding of the \(\text{AlS}^-\) and \(\text{AlCl}^-\) species is “chemical” in nature. This word chemical is undefined in this context. In addition, there are no analyses of the energetics of these species to support any bonding type. Indeed, however unlikely it is, one can have \([\text{AlCl}_4]^-\) ions in solution even of the non-coulombic type. If “chemical” is defined as non-coulombic interactions then, of course, noncoulombic forces are undoubtedly significant but they are likely to be smaller than the large coulomb forces involved (unless sulfide ions in solution lose charges close to zero). To the important, the noncoulomb energy of interaction of \(\text{Al}^{14+}\) with a nearest neighbor chloride ion must be more negative than the noncoulomb energy of interaction of \(\text{Al}^{14+}\) with a nearest neighbor sulfide ion by an amount close in magnitude to the coulomb energy. This seems unlikely but, of course, is not impossible. Quantum mechanical calculations of the energetics of these species are underway.

The average coulomb complex has an unknown and generally unspecified number of alkali and chloride ions of the solvent as near neighbors. To do as Berg and Bjerrum have done and select out a small number of solvating chlorides (or part of the complex is speculative and may not represent the real species, which could readily have a broad distribution of different ionic environments which could be extremely difficult, if not impossible to observe by any known structural measurement. From a thermodynamic point of view, the solvent ions in the environment are irrelevant if both \(\text{Al}^{14+}\) and \(\text{S}^-\) at low concentrations.

Berg and Bjerrum do bring out an important point concerning larger complexes. Although we felt that the evidence favored the simple \(\text{AlS}^-\) complex (albeit solvated by solvent cations and anions), we could not rule out the importance of larger species as we stated in our paper. It is unfortunate that Berg and Bjerrum contribute to the confusion concerning the differences between complexing in additive binary systems (e.g., \(\text{K}^+\), \(\text{Al}^{14+}/\text{Cl}^-\)) and in reciprocal systems (e.g., \(\text{K}^+\), \(\text{Al}^{14+}/\text{Cl}^-\), \(\text{S}^-\)). In the first case, all cations are “complexed” and one considers as “true” complexes those special and presumably tightly bound species whose structural data are available to define the structure. Of all the binary chlorides in binary systems, there is no known \(\text{Al}^{14+}\) species that can be identified as a true complex. All ions are probably the clearest examples of systems with “true” complexes. For a major fraction of binary chloride systems, there is some uncertainty and there are many shades of gray. Even for the “true” complexes, the structural information by itself says nothing about the energetics and type of bonding which might even be largely ionically.

Thus, evidence for the existence of a complex is of no value in understanding the energetics of reaction of \(\text{Al}^{14+}\) ions with sulfide or oxide ions. In reciprocal systems at low concentrations of solute cations and anions, a complex is formed between the solute ions when they are each others nearest neighbors with a greater than random distribution of configurations of the solvent ions about the separated solute ions and about the complex are usually not considered in defining such complexes. This type of complex is less subject to uncertainty in definition than the type in additive systems. Our point is that the coulomb attractions between \(\text{S}^-\) (or any other species) and \(\text{Al}^{14+}\) in aqueous solutions (or in the polymerizations of anions and polynuclear ions under the use of molecular dynamics and quantum mechanical calculations under development for calculating the influence of shielding and of noncoulomb forces: If non-coulomb (e.g., covalent) forces are important they could even enhance the effects we discussed. By contrast, Berg and Bjerrum do not offer any testable alternative.

\(^{40}\) L. A. Curtiss, Personal communication.

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