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CHEMICAL AND ELECTROCHEMICAL STABILITY OF SOME MOLYBDENUM COMPOUNDS IN MOLTEN ALKALI ELECTROLYTES

Mihai V. POPA, Cristina DONATH, Niculae ENE* and Elena NEACŞU

Roumanian Academy, Institute of Physical Chemistry "Ilie Murgulescu"
Spl. Independentei nr. 202, 060021, Bucharest, Roumania

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The stability of some molybdenum compounds (K_3MoCl_6, MoO_3, and K_2MoO_4) has been studied in eutectic NaCl-KCl-NaF molten electrolyte at 1023 K by different complementary analytical and electro-chemical techniques, using tungsten and molybdenum wire as working electrode and Ag/AgCl as reference electrode. It was indicated that MoO_3, in contrast to K_3MoCl_6, or K_2MoO_4, interact with molten electrolyte. The product of this interaction is complex oxo-anion, probably in the form of $[MoO_3Cl_2]^{2-}$. In case of K_3MoCl_6 the variations of the open-circuit potentials of working electrode (Mo), vs. reference electrode, recorded during several hours (from 0.396 V at time = t_0 to 0.224 V at time = t_0 + 240 minutes) showed that electrolyte containing K_3MoCl_6 at bellow $2\cdot10^{-4}$ mol/cm^3 was not stable. Unlike the behavior described above, the electrolyte that contains K_3MoCl_6 at a concentration equal or higher that $4\cdot10^{-4}$ mol/cm^3 is stable (open-circuit, 0.519 V ± 0.001 V, is constant).

INTRODUCTION

Interest in refractory metals of the group IV, V and VI in general and molybdenum in particular, with their high melting points, good thermal properties and excellent mechanical properties, has increased rapidly with the advent of the missile, space industries and modern military technologies.[1] Molybdenum, however, appears to be dangerously close to exhaustion and has consequently been classified as a strategically sensitive material.[2] Conservation of molybdenum may thus become a priority. However, the production methods, such as compact powder sintering and arc casting, are expensive and useful forms of molybdenum metal are difficult to fabricate. The electrodeposition of molybdenum from molten salts is of considerable interest for the following reasons. (1) Molybdenum cannot be electrodeposited from aqueous solution; (2) Since molybdenum is generally scarce and expensive, it is more desirable to use them as a thin coating on the appropriate substrate or an electroform rather as a bulk.[3-5]

Molybdenum has been electrodeposited from a variety of molten electrolyte systems including fluorides,[6] chlorides[7-10] and mixed electrolytes,[11-14] but for practical applications, chemical and electroche-mical stability of these systems is the most important factor. To our knowledge, the chemical stability of molybdenum compounds in these systems has not been investigated, and this paper deals with the study of the stability of some molybdenum compounds in molten KCl-NaCl-NaF eutectic at 1023 K, by electro-chemical and analytical techniques.

EXPERIMENTAL

The NaCl-KCl-NaF eutectic (60,5-22,5-17 mol %, m.p. 879 K) was prepared from alkali halide of analytical grade and was dehydrated by heating under vacuum according to the procedure recommended in the literature.[15]

All the electrochemical measurements were performed at 1023 ± 5 K in a conventional three-electrode cell using a computer-controlled potentiostat model Tacussel PRT 20-10X. Open circuit voltage measure-ments, linear sweep voltammetry and chemical analysis were employed. The electroactive molybdenum concentration was determined by linear sweep voltammetry, by measuring the reduction peak current (these results had an overall accuracy of ±10%, due to difficulties in estimating the active surface area of the electrode) and the chemical analysis. Chemical analysis was performed using a Chroma Colorimeter model 252 Analoque Colorimeter. Data

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* Corresponding author: nene@chimfiz.icf.ro

were recorded using a Linseis recorder model LY 1600. The working electrode used was a tungsten wire (1 mm diameter) for the voltammetric determinations and molybdenum wire (1 mm diameter) for open-circuit determination. The reference electrode was a silver wire dipped in a solution of AgCl in KCl-NaCl-NaF ($1.12\cdot10^{-3}$ mol/cm^3) separated from the working electrolyte by a thin BN membrane.

RESULTS AND DISCUSSION

The cell used to measure the open-circuit potential between cathode and reference electrode was of the following type:

$$(-)\ Mo \left| \underset{in\ electrolyte}{MoX\ (x_1)} \right\| \underset{membrane}{BN} \left\| \underset{in\ reference}{AgCl\ (x_2)} \right| Ag\ (+) \tag{1}$$

The reaction for a cell of the type shown above is:

$$Mo\,(s) + [n\,Ag^{+}(AgCl\ in\ reference)] = [Mo^{n+}(MoX\ in\ electrolyte)] + n\,Ag\,(s)$$

where: MoX (x_1) is molybdenum compound with molar fraction x_1 dissolved in molten electrolyte and $(\mathrm{MoX})^{n+}$ it's corresponding cation; $AgCl$ (x_2) is molar fraction of AgCl in Ag/AgCl reference.

$\underset{membrane}{BN}$ is membrane made from Boron Nitrite

The relationship between the cell potential and molybdenum concentration in the electrolyte is given by the Nernst equation in the expanded form:[16]

$$E = E^{o}_{Ag^{+}/Ag} - E^{o}_{(MoX)^{n+}/Mo} + 2{,}303\,\frac{RT}{nF}\log\frac{x_1}{(x_2)^{n}} - 2{,}303\,\frac{RT}{nF}\log\frac{\gamma_2}{\gamma_1^{n}}$$

where: $E^{o}_{(MoX)^{n+}/M}$ is standard electrode potential of the Mo in molybdenum compound;

c_{MoX}, γ_2 are, respectively, Mo concentrations and mean activity coefficients in the cell;

$E^{o}_{Ag^{+}/Ag}$ is the standard electrode potential of Ag in reference electrode.

The results of open-circuit E ($E = E_{cathode} - E_{anode}$) measurements with this cell at different molybdenum compounds are given in Figs. 1 and 2.

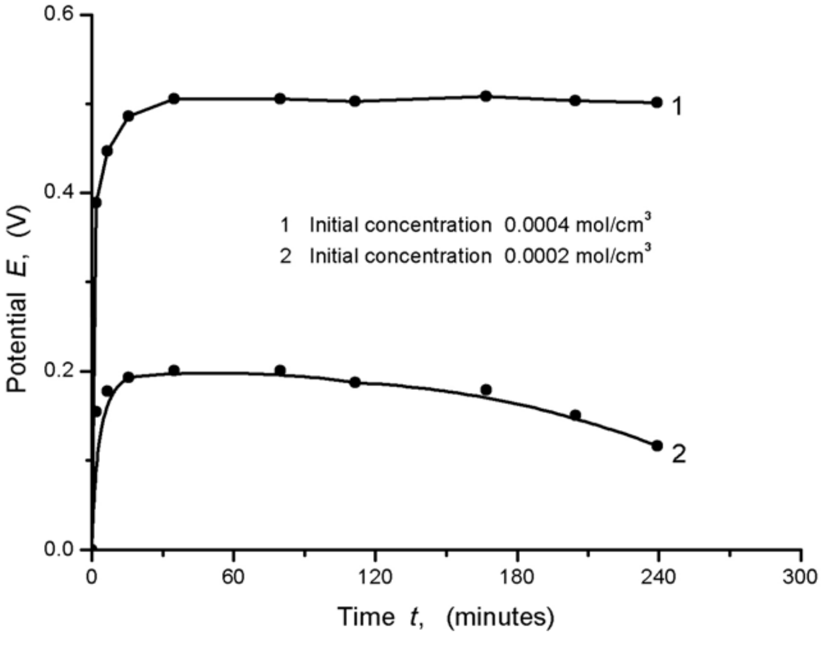

Fig. 1 – Open-circuit potential vs. time in NaCl–KCl-NaF-K_3MoCl_6; $S_{cat} = 7{,}8\cdot10^{-3}$cm^2.

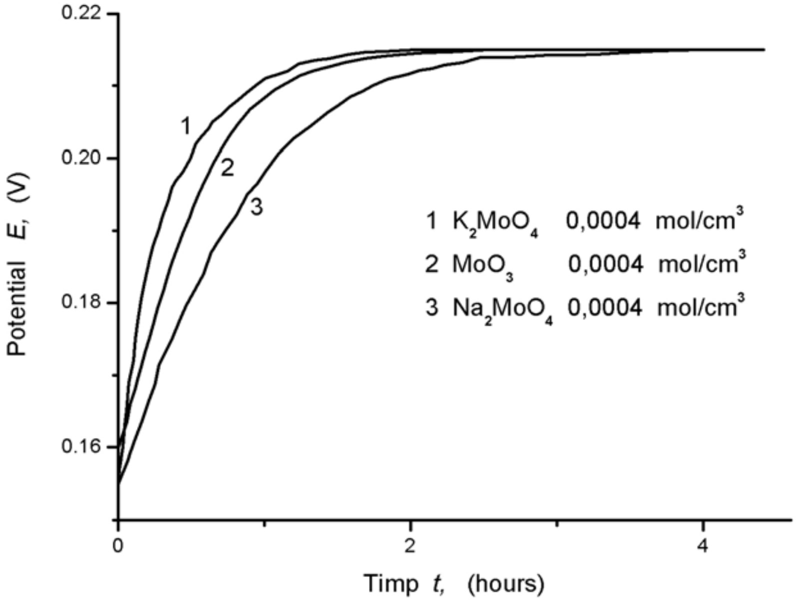

Fig. 2 – Open-circuit potential vs. time in NaCl–KCl–NaF–(MoO) compounds; $S_{\mathbf{cat}} = 7{,}8\cdot10^{-3}$cm^2.

It was found that the open-circuit potential is monotonously increasing, although the slope of this increase depends on the chemical nature of the molybdenum compound. Thus, as shown by the analysis of the data from Fig. 2, this slope may be constant or may change during the experiment.

At concentrations higher than $4\cdot10^{-4}$ mol/cm^3 the electrolyte is stable and the steady-state is reached rather quickly, *i.e.* in about 45 minutes after adding the solute into the molten electrolyte. Conversely, at low concentrations (below $2\cdot10^{-4}$ mol/cm^3) the steady-state is not reached. In this case, the sharp increase of the potential (that reaches its maximum value after ca. 15 minutes) is followed by a slow but continuous decrease. At this stage, the reason for this behaviour is still unclear. We could assume, however, that this is either the effect of some adsorption processes of K_3MoCl_6 on the cell walls, or the result of the formation of insoluble compounds that contain oxo-chloro anions of molybdenum. There are reasons to believe that these compounds could occur from chemical reactions with traces of oxygenated species from the electrolyte, most likely solid $MoOCl_3$ or dissolved $[MoOCl_4]^-$.[17] An alternative explanation is provided by assuming that the following disproportionate reactions may take place:

$$(MoCl_6)^{-3}_{solutie} \rightarrow (MoCl_3)_{solutie} + 3Cl^-$$

$$5\ (MoCl_3)_{solutie} \rightarrow 2\,Mo_{solid} + 3(MoCl_5)_{gaz}$$

or

$$5[(MoCl_6)^{3-}]_{solutie} \rightarrow 3[MoCl_5]_{solutie} + 2\,Mo_{solid} + 15\,Cl^-_{solutie}$$

These reactions are favorized by the low concentration of K_3MoCl_6. This assumption was firstly made by Senderoff[5] and was confirmed by the results reported later by Gabriel.[6]

A different situation is encountered when both an oxygenated compound of molybdenum and B_2O_3 are dissolved in the molten electrolyte. In this case, as data from Fig. 3 shows, the potential increases and then, after reaching a maximum slowly decreases to a constant value. We can assume that, in the first stage, the increase of the potential is due to a gradual dissolution of the oxygenated compounds of both boron and molybdenum. This process is followed by the formation of complex compounds (in which B and Mo species are involved) that is responsible for the decrease of the potential down to a plateau. One may notice that these processes are rather slow, as evidenced by the fact that the steady-state value of the potential is reached in about 120 minutes after adding the two compounds into the molten electrolyte.

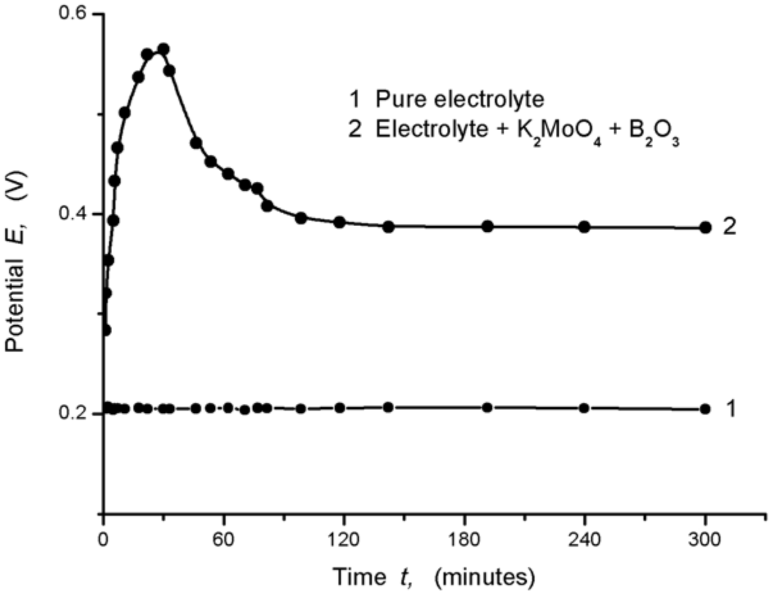

Fig. 3 – Variation of open-circuit potential with time in electrolyte NaCl–KCl–NaF–K_2MoO_4–B_2O_3:
$C_{K_2MoO_4}$ = 4·10^{-4} mol/cm^3; $C_{B_2O_3}$ = 2·10^{-3} mol/cm^3 ; T = 1023 K; cathode = Mo.

The voltammograms in Fig. 4, illustrating the variation of the current as a function of the time elapsed from the K_3MoCl_6 addition, also put into evidence the stability of the electrolyte.

It was found that, within the limit of the experimental errors, the cathodic peak current gradually decreases by increasing the time after which the corresponding voltammograms is recorded. Because the experimental conditions were the same, and because one cannot assume any change of the value of the diffusion coefficient or of the activity of the molybdenum ions, it appears that the decrease of the cathodic peak current is only the result of a change of the Mo ions concentration (see Table 1). This also proves the chemical instability of the investigated electrochemical system. By using Sevcik-Randles equation,[18] after 4 hours from the addition of K_3MoCl_6, a decrease of its concentration was found, from 2·10^{-4} to 0.19·10^{-4} mol/cm^3, in good agreement with analytical determination.

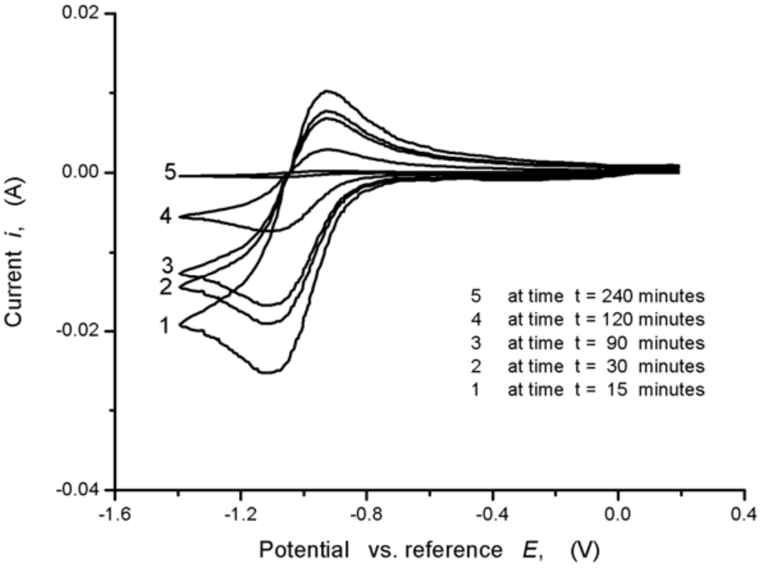

Fig. 4 – Variation of current with time in electrolyte NaCl–KCl–NaF–K_3MoCl_6:
$C_{K_3MoCl_6}$ = 2·10^{-4} mol/cm^3; v = 20 mV/sec; T = 1023 K; cathode = W; $S_{\mathbf{cathode}}$ = 7,8·10^{-3} cm^2.

Table 1

Variation of peak current with the time elapsed from the K_3MoCl_6 addition

Compound	Time (minutes)	Peak current – i_p (mA)	K_3MoCl_6 mol/cm^3
K_3MoCl_6	15	25.48	$2.0\cdot10^{-4}$
	30	19.24	$1.49\cdot10^{-4}$
	90	16.87	$1.30\cdot10^{-4}$
	120	7.34	$0.57\cdot10^{-4}$
	240	0.56	$0.19\cdot10^{-4}$

The cyclic voltammograms in Fig. 4 exhibit one peak in the cathodic run at about – 1.114 V versus reference electrode. The height of the peak at – 1.114 V attributed to the electrochemical reduction of the molybdenum (III) ions:

$$[MoCl_6]^{3-}_{(liq)} + 3e^- \rightarrow Mo_{(s)} + 6Cl^-_{(liq)}$$

increases with the molybdenum ion content.

The intensity of the cathodic peak is correlated with the scanning rate of potentials by the following relationship, reliable for a reversible soluble system[18]:

$$I_p = -6.34\cdot10^6\, n^{3/2} S C^o\, T^{-1/2}\, D^{1/2} v^{1/2}$$

where ***S*** is the electrode area (cm^2); ***C*°** the solute concentration (mol/cm^3); ***D*** the diffusion coefficient (cm$^2\cdot$s^{-1}); ***n*** the number of exchanged electrons; ***v*** the potential scanning rate (V$\cdot$s^{-1}) and ***T*** the temperature in K. The linearity of I_p versus $v^{1/2}$ (Fig. 5) proves that the electrochemical reduction process is controlled by the diffusion of molybdenum ions in the electrolyte.

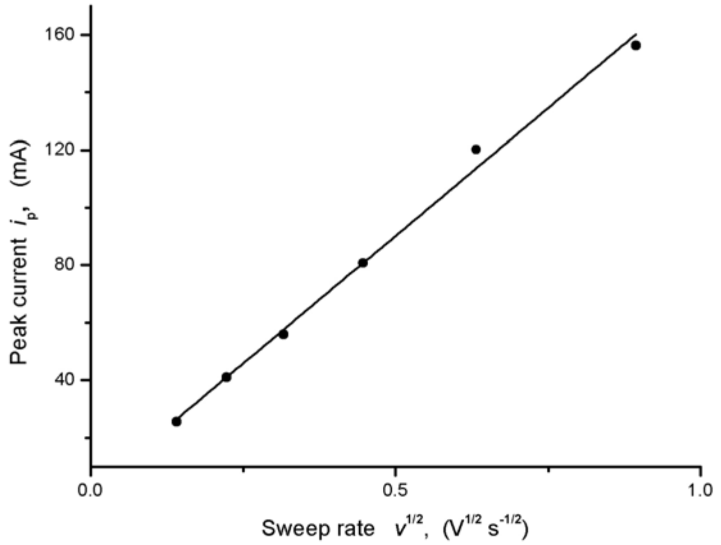

Fig. 5 – Linear relationship of Mo(III) reduction peak current density vs. the square root of the scanning potential rate in electrolyte NaCl–KCl–NaF–K_3MoCl_6:
$C_{K_3MoCl_6} = 2\cdot10^{-4}$ mol/cm^3; T = 1023 K; cathode = W; $S_{\mathbf{cathode}} = 7{,}8\cdot10^{-3}$ cm^2.

In the case of NaCl-KCl-NaF electrolytes that contain simple or complex oxygenated molybdenum compounds (MoO_3 or K_2MoO_4, respectively) as dissolved species, the stability was also found to be remarkably good.

Thus, as data from Table 2 indicate, in these electrolytes there are not chemical reactions preceding the electrochemical process that takes place at the electrode.

It was observed that within the investigated time range the value of the cathodic peak current is constant proving that, under the same experimental conditions, the concentration of the Mo ions from the solution is also constant. The values of the concentration of the molybdenum ions in the molten system NaCl-KCl-NaF-MoX, as estimated by quantitative chemical analysis (see Table 2) also support the above results concerning the stability of this system.

Table 2

Variation of peak current (determined from voltammograms – not shown) with the time elapsed from the oxygenated molybdenum compounds addition

Compound	Time (minutes)	Peak current (mA)
MoO_3 $2\cdot10^{-4}$ mol/cm^3	15	22.28
	30	22.32
	90	22.30
	120	22.35
	240	22.31
K_2MoO_4 $2\cdot10^{-4}$ mol/cm^3	15	22.13
	30	22.33
	90	22.28
	120	22,40
	240	22.36

It was observed that within the investigated time range the value of the cathodic peak current is constant proving that, under the same experimental conditions, the concentration of the Mo ions from the solution is also constant.

The values of the concentration of the molybdenum ions in the molten system NaCl-KCl-NaF-MoX, as estimated by quantitative chemical analysis (see Table 3) also support the above results concerning the stability of this system.

Table 3

Concentration of molybdenum ions in the molten system NaCl-KCl-NaF-MoX as a function of the time elapsed from the MoX compounds addition

Compound	Time (minutes)	Concentration (10^{-4} mol/cm^3)
MoO_3 $4\cdot10^{-4}$ mol/cm^3	15	0.9
	30	1.3
	90	3.1
	240	4.1
K_2MoO_4 $4\cdot10^{-4}$ mol/cm^3	15	1.9
	30	3.1
	90	4.1
	240	3.9
K_3MoCl_6 $4\cdot10^{-4}$ mol/cm^3	15	1.1
	30	3.5
	90	4.1
	240	4.0

CONCLUSIONS

From the results obtained thus far, one may draw the conclusion that the molten systems NaCl-KCl-NaF-MoX (where MoX stands for an oxygenated compound of molybdenum) exhibit remarkable stability, regardless the concentration of Mo species in the electrolyte. In these systems, the dissolution of simple oxygenated molybdenum compounds is more rapid compared to that of complex ones. Nevertheless, this behaviour could be also a result of the preparation conditions, among which the treatment temperature and the specific surface are of the powder are the most important. It was also observed that for electrolytes in which a halogenated complex compound (K_3MoCl_6) is dissolved, the stability of the electrochemical system is controlled by the concentration of that particular compound.

REFERENCES

1. R. W. Holliday, in “Molybdenum”, from “Mineral Facts and Problems”, US Bureau of Mines, Bulletin 630, New York, 1965, p. 595-678.
2. I. A. Bucklow, in “Coatings for High Temperature Applications”, Applied Science Publishers, London, 1983, p. 139-154.
3. S. Senderoff and G. W. Mellors, *Science*, **1966**, *153*, 1575-1582.
4. K. Koyama, Y. Hashimoto and K. Terawaki, *J. Less Common Metals*, **1986**, *123*, 223-231.
5. K. Koyama, Y. Hashimoto, S. Omori and K. Terawaki, *J. Less Common Metals*, **1987**, *132*, 57-64.
6. J. C. Gabriel, D. Vincent and T. Griffiths, Electrochimica. *Acta*, **1999**, *44*, 4619-4629.
7. J. C. Gabriel, J. Bouteillon and J. C. Poignet, *J. Electrochem. Soc.,* **1994**, *33*, 2286-2292.
8. S. Senderoff and G. W. Mellors, *J. Electrochem. Soc.*, **1965**, *112*, 266-274.
9. S. Senderoff and G. W. Mellors, *J. Electrochem. Soc.*, **1965**, *112*, 840-848.
10. S. Senderoff and G. W. Mellors, *J. Electrochem. Soc.*, **1966**, *113*, 66-72.
11. S. Senderoff and G. W. Mellors, *J. Electrochem. Soc.*, **1967**, *114*, 586-592.
12. G. Li and D. Fan, *Mater. Sci. Forum,* **1991**, *73-75*, 443-448.
13. Ye Shangyun and Li Guoxun, *Rare Metals*, **1991**, *10*, 15-23.
14. McCawley Frank and W. Charlie, *J. Electrochem. Soc.,* **1969**, *166*, 1208-1212.
15. G. J. Janz, in “Proceeding of the Third International Symposium on Molten Salts”, The Electro-chemical Society, New Jersey, 1981, p. 52-57.
16. S.N. Flengas and T. R. Ingraham, *J. Electrochem. Soc.,* **1958**, *106(8)*, 714-721.
17. S. H. White and U. M. Twardoch, *J. Appl. Electrochem*., **1987**, *17*, 225-231.
18. R. N. Adams, in “Electrochemistry at Solid Electrolytes”, Marcel Dekker, New York, 1969, p. 127-133.