CANDIDATE MATERIALS FOR THE SULFUR ELECTRODE
CONTAINER/CURRENT COLLECTOR
CERAMIC OXIDES

R. P. Tischer and H. Wroblowa
Advanced Components and Energy Systems

G. M. Crosbie and G. J. Tennenhouse
Ceramic Materials Department
Research Staff
Ford Motor Company
Dearborn, Michigan 48121

SUMMARY

In the search for materials for the container/current collector of the sulfur electrode in the sodium-sulfur cell, several chromium oxide based candidates for possible use as coatings have been tested. Samples of chromium oxide doped with Li$_2$O, MgO, NiO and Ta$_2$O$_5$ have been produced and characterized. The only n-type oxide - Ta$_2$O$_5$ - was rejected, a priori, owing to its high initial resistivity. Corrosion tests were carried out at 350°C in small laboratory cells using the bulk oxide samples as test electrodes. The latter were exposed to the extremes of electrochemical conditions to which the container/current-collector might be locally exposed in a practical Na/S cell for periods of time up to ~6 months. Surface attack was found to be negligible. However, an increase of bulk resistivity of the samples and of overpotential was observed in all cases. The increase of resistivity is attributed to the loss of carriers in the p-type semiconductor oxides, caused by equilibration of the latter with the negligible partial pressure of oxygen in the reducing atmosphere of the sulfur-polysulfide melt at 350°C. The increase of overpotential is interpreted in terms of the loss of the electroactive surface area due to, among other reasons, the accumulation of sulfur or solid lower sulfides at the interface and/or changes of its adsorptive properties.

Potential candidate materials are Li$_2$O-doped and MgO-doped Cr$_2$O$_3$. 
I. Introduction

Secondary batteries employing molten sulfur electrodes must operate above the melting point of sulfur (113°C) and of the medium containing the sulfur ions ($> 300^\circ$C in the case of sodium polysulfides $\text{Na}_2\text{S}_x$, where $3 < x < 5$). At the upper end, the practical operating temperature is limited to ~400°C by the increasing vapor pressure of sulfur. Material problems, i.e., accelerated corrosion of electrodes, of the container/current collector, and seals also become more severe with increasing temperature. Container corrosion can have diverse effects. Apart from attacking the material and consuming active reactant (thereby reducing capacity), it forms surface layers that increase contact resistance to the felt electrode. Also soluble corrosion products can be redeposited, clogging the felt electrode, obstructing transport of active materials, and causing uneven current distribution. If deposited on the electrode surface, they may change its structure and wettability and therewith the kinetics of reactions occurring at this surface to the point where it may become partially or completely blocked. Corrosion products can also be deposited on the surface of the solid electrolyte partially blocking, damaging or destroying it by causing locally excessive current densities or by direct interaction or penetration.

Few conductive materials can withstand the attack of the polysulfide melt at the operating temperature of the Na/S cell. Metals are thermodynamically unstable. They form sulfides, whose solubility in the polysulfide/sulfur melt is, in most cases, not negligible. Some metals like chromium, molybdenum, tungsten, and aluminum become covered by protective layers which, however, lose their passivating properties under certain conditions. Among electronically conductive materials which have been reported, or are expected, to resist polysulfide melt attack are various forms of carbon, certain oxides, carbides, nitrides, and conductive glasses.

This part of the ongoing study involves doped chromium oxides.

II. Corrosion in Polysulfide/Sulfur (PS) Melts

Chromium oxide has been chosen as the base for candidate coating materials in view of the prior experience of corrosion stability of $\text{Cr}_2\text{O}_3$ under static conditions (1).
III. Required Coating Characteristics

The necessary coating characteristics consist of inherent material properties:

- Corrosion stability of the doped material interfacing with the polysulfide (PS) melt, when exposed to the wide range of the interfacial potential drops encountered in a practical Na/S cell.

- Sufficient and stable conductivity, such that the resistance of the coating is negligible in comparison with that of the entire Na/S cell. The percentage of the power loss as a function of material resistivity and coating thickness is shown in Fig. 1.

![Fig. 1](image)

Fig. 1  Power loss as a function of material resistivity and coating thickness for a 230 cm² container and for 0.02 Ω cell resistance due to all other sources.

- Preferential wettability for sodium polysulfide rather than sulfur.

In addition to these inherent material properties, coatings must also have the following characteristics:

- Adherence to the substrate under conditions of thermal and electrothermal cycling.

- Impermeability.
Cost-viability, involving primarily a cheap production method of deposition on a self-healing substrate, i.e., one which passivates upon exposure to the melt.

IV. Conductivity of Oxides Studies

Doped Chromium Oxides

A reliable value of the resistivity of air-annealed polycrystalline Cr₂O₃ (97+% dense, total impurity less than 0.01%) at 350°C is reported as 410 Ωcm (5). The interpretation of the electronic resistivity of highly pure Cr₂O₃ in terms of defects, their concentrations, and mobilities remains incomplete. Lower partial pressures of oxygen (below 1125°C) cause higher resistivities. This, together with the sign of the thermoelectric coefficient, implies p-type conduction.

Impurities of p-type, such as NiO, appear to be charge compensated by electron holes (high p₀₂) or oxygen vacancies (low p₀₂). Thus, p-type dopants tend to enhance electronic conductivity after an air anneal.

A substantial increase in the conductivity of air annealed Cr₂O₃ (above 400°C) by doping with NiO (7,8) and MgO (7,9) has been reported. Literature data concerning the conductivity of Li₂O doped Cr₂O₃ are inconclusive (6,10). Other dopants are reported either to increase the resistivity (Nb₂O₅ (7,9,10) TiO₂ (7,8,11) WO₃ (8)) or to have little or no effect (Al₂O₃ (10), Fe₂O₃ (7), ZnO (8)).

V. Experimental

A. Materials

A separate paper on the preparation and characterization of doped chromium oxides will be published (presented at the April 1983 meeting of the American Ceramic Society).

B. Apparatus

Test Procedure

The corrosion test cell (Fig. 2) consisted of a glass vessel provided with graphite counter and reference electrodes and a graphite rod to which the test sample was dove-tailed and fastened by Dylon graphite cement. The contact resistance of this connection was negligible. The cell had a separate outlet for evacuation.

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The corrosion tests were preceded and followed by ex situ measurements of sample resistivity as a function of temperature, using the AC method at 1.6 and 20 kHz.

The surfaces of the samples were examined before and after the corrosion tests by means of SEM,* EDAX,** and AES.***

The cell was assembled by fitting the electrodes and the thermocouple-well into the silicone stopper. A weighed amount of sodium polysulfide was filled into the cell in the dry box. Before heating in the furnace, the pressure in the cell was reduced to about 60 kPa by a vacuum system filled with prepurified argon to prevent backstreaming of air into the cell. Cells were tested at 350°C.

* SEM — Scanning electron microscopy
** EDAX — Energy dispersive analysis of x-rays
*** AES — Auger electron spectroscopy
The samples were either exposed to cathodic or anodic polarization at various current densities and periods of time, or cycled at the desired current densities with a frequency of 5 cycles/day. The resistive contribution to the sulfur electrode potential was monitored by the AC and/or the interrupt method.

VI. Resistivites of Test Materials

These resistivities at 350°C are shown in Table I. The values given are measured with 20 kHz AC, and they are within 3% of the 1.6 kHz values in all cases. The capacitive contribution (phase shift) was negligible at both frequencies.

| Mol % dopant | Li2O | MgO | NiO | Ta2O5 |
|--------------|------|-----|-----|-------|
| Cr2O3 - CP   |      |     |     |       |
| 0            | 530  | 2.5 | --  | --    |
| 0.1          | --   | --  | 16.0| --    |
| 0.2          | 66.  | 4.3 | --  | --    |
| 0.5          | 162  | 3.8 | 3.8 | --    |
| 1.0          | 4.3  | 5.0 |     |       |
| 2.0          | --   | --  | 2.5 | --    |
| Cr2O3 - HP   |      |     |     |       |
| 0.5          | 4.4  | 2.6 | 3.2 | 470   |
| 4.0          | 152  | 4.3 |     |       |

a) Air-annealed as a 2.5 mm thick bar.
Dopant homogeneity is likely to improve with the exposure of the oxide to an oxidizing environment, and such treatment would be expected to cause a shift of positive defect types from ionic ones (such as oxygen vacancies, which are likely needed for low-oxygen-pressure sintering, or chromium interstitials) to electron holes.

Resistivities considered acceptable (<100 $\Omega$cm) were achieved in all samples (Table I), except CP - $Cr_2O_3$ without dopant, HP - $Cr_2O_3$ with $Ta_2O_5$, and CP - $Cr_2O_3$ with $Li_2O$. (CP: chemically pure, HP: high purity)

As an example, the resistivity of the as-oxidized NiO doped series is shown (Fig. 3) to follow a simple pattern in spite of different oxide purity level (HP and CP) and variations in density and grain size: a higher dopant level produces a lower resistivity. The approximate linearity suggests that the solubility limit for NiO is not passed.

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**Fig. 3** Resistivity of NiO-doped Cr$_2$O$_3$ at 350°C. Each symbol denotes bars from one hot pressing.
VII. Method of Testing Material Suitability

The corrosion tests, as a rule, involve bulk samples in order to separate the inherent material suitability from complications arising due to poor adhesion and/or porosity of coatings. Also, the development of an lengthy adequate coating method is a difficult task, and bulk testing allows the elimination of unsuitable materials at an early stage.

The bulk samples are tested as electrodes polarized in sodium polysulfide (PS) melt at 350°C.

The exposure of the sample to the PS melt is accompanied by extremely fast Faradaic redox reactions of the sulfur system. Therefore corrosion currents cannot be observed directly. Electrochemical measurements can only indicate changes in the apparent resistance, which may be due to

a) changes of the resistance of the part of the circuit comprising the test and reference electrodes, and the PS melt,

and/or

b) changes of overpotential, reflecting the loss of electroactive surface area and/or change of the adsorptive properties of the interface.

Re a): The ohmic component involves primarily the ohmic drop, \( I_{Re} \), in the oxide electrode. The remaining part (i.e., the resistance of the electrolyte between the test and reference electrodes, as well as that of the current leads) is constant and negligible as compared with \( R_e \).

Re b): The overpotential consists mainly of concentration polarization. Therefore, a change of the melt composition in the immediate vicinity of the test electrode will result in a change of potential at constant current. An increase of activation overpotential may be observed due to the accumulation of reaction products blocking large parts of the surface.

The suitability of the tested sample has to be inferred from a) the observed changes in resistance and overpotential (at constant current) as a function of time and electrochemical treatment; b) comparison of the surface by optical, SEM, and spectroscopic methods before and after the experiment.

It follows that the acquisition of the electrochemical data necessary to evaluate the sample requires
1. Separation of the ohmic potential drop from the electrode overpotential. This is accomplished by monitoring the test electrode resistance, $R_e$;

2. Establishment of the real current density at the tested sample. Owing to the high resistivities of ceramic oxides, the current distribution along the sample may not be uniform, and therefore the apparent average density of the polarizing current does not represent the real situation.

In Fig. 4 the approximate equivalent circuit of the test cell is shown, on which the calculation of the current distribution at the test sample as a function of its resistivity is based (similar calculations have been previously reported (12)).

**Fig. 4** Approximate equivalent circuit of the test cell under current.

$R_p$ - resistance of the melt per unit length of tested sample, $\Omega/\text{cm}$

$R_s$ - resistance of tested sample per its unit length, $\Omega/\text{cm}$

$V$ - steady state voltage,

$i_k$ - current increment, $\partial I/\partial x$, in the element "k", $A/\text{cm}$
Solving \((n + 1)\) Kirchhoff equations one arrives at the equation

\[
(I_{n+1} - I_n) - (I_n - I_{n-1}) = (R_S/R_p) I_n
\]

where \(I_k = I_k/I_T = dI(x)/dx\), \(I_x = I_x/I_T\), \(x = x/L\),

\(R_S\) = resistance per unit test-sample length,
\(R_p\) = effective melt resistance per unit length of test sample,

\(L\) = length of the immersed electrode,

\(I_T\) = total current.

The solution of eq. (1), rewritten in the form

\[
I'' - (R_S/R_p) I' = 0
\]

is given by

\[
I_x = \text{sinh} \left( \frac{x R_S}{R_p} \right) / \text{sinh} \left( \sqrt{R_S/R_p} \right)
\]

which represents the current profile along the electrode. The task is to find the part of the electrode length \(x\), which practically carries no current, e.g. \(I_x < 0.1\). Introducing the latter condition into eq. (3) and solving for \(x\), one obtains

\[
x = \sqrt{R_p/R_S} \sinh^{-1} \left[ 0.1 \sinh \sqrt{R_S/R_p} \right]
\]

Then the electrode length which has to be taken into account in evaluating the current density is given by

\[
1 - \bar{x} = 1 - \sqrt{R_p/R_S} \sinh^{-1} \left[ 0.1 \sinh \sqrt{R_S/R_p} \right]
\]

The plot of the percentage of the electroactive electrode area as a function of \(\sqrt{R_S/R_p}\) (lower scale) is shown in Fig. 5. On the upper non-linear abscissa scale resistivities of the test materials are indicated (which take into account the resistivity of the melt and the geometry of the test cell).

It can be seen that for the doped \(\text{Cr}_2\text{O}_3\) samples \((\rho > 50 \, \Omega\text{cm})\) over 90% of the current is carried by only \(~6\%\) of the electrode area.
Fig. 5 Percent of the electrode area which carries 80, 90, 95 and 99% of total current as a function of $\sqrt{R_c/R_p}$ (lower scale) and material resistivity (upper scale). $R_c$ resistance of the electrode, $R_p$ resistance of the electrode (Ωcm⁻¹).

VIII. Results and Discussion

Ceramic oxide samples were exposed to polysulfide melt at 350°C for periods of time of up to 6 months. During this time they were polarized anodically, cathodically, and/or cycled at current densities sufficient to expose the sample surface to the entire span of melt compositions between sulfur and Na₂S₃, to which parts of the container (current collector) can be exposed locally.

No signs of corrosion have been observed either by surface examination (SEM, EDAX, AES) (exemplified by Fig. 6) or by analysis of the melt carried out using ICP (inductively-coupled plasma) atomic emission spectroscopy. Results of the latter analyses showed negligible traces of the elements present in the sample to be dissolved in the melt even after 150 days of exposure (10 – 20 ppm).
Fig. 6 SEM-photographs of sample surfaces before and after test.

Fig. 7 Resistivity change with time during test of doped Cr$_2$O$_3$ samples.
However, all samples showed changes in their electrochemical behavior in that both the resistive and the other components of overpotential varied with time.

A. Resistivity as a Function of Time

The resistivity of all materials changed with time, as shown in Fig. 7 for doped \( \text{Cr}_2\text{O}_3 \). This behavior seems to be independent of polarization, since the resistivity of a non-polarized \( \text{MgO} \) doped \( \text{Cr}_2\text{O}_3 \) sample also increased upon exposure to \( \text{Na}_2\text{S}_5 \) melt (cf. Fig. 7). In the case of \( \text{Li_2O} \) doped HP-\( \text{Cr}_2\text{O}_3 \) and \( \text{MgO} \) doped \( \text{Cr}_2\text{O}_3 \), the resistivities eventually stabilized at values about 60 \( \text{Ohm} \), measured in situ.

There was the possibility that the resistance increase was due to surface leaching of the dopant. However, this proved not to be the case. The phenomenon was found to be 1) a bulk effect (abrating the surface layer did not improve the conductivity of the sample as measured ex situ or in situ after reintroduction into a new cell), 2) resulting from exposure to the melt (cf. Table II, AC) as well as from exposure to sulfur vapor only (cf. Table II, AE), or to a low \( \text{P}_{\text{O}_2} \) in the absence of sulfur (cf. Table II, AF), 3) reversible (ex situ) by a 6 h anneal in air at 1500°C, i.e., by repeating the pretreatment of hot pressed oxides (cf. Table II, AD and ADA, AC and ACA).

This leads to the conclusion that the reducing atmosphere of a sulfur or polysulfide environment (in which the sample tends to equilibrate with an extremely low partial pressure of oxygen) results in an increase of oxygen vacancies and a concurrent decrease in the number of holes (carriers), and therefore of conductivity.

B. Overpotential (at Constant Current) as a Function of Time

The overpotential, remaining after deducting the IR drop from the total polarization, also shows an increase with time, for which there are three possible mechanisms.

1) Part of this increase is due indirectly to the rise in sample resistance. This reduces the effective surface area of the sample (cf. Fig. 5) and thereby increases the current density.

2) An increase in polarization may also be caused by accumulation of reaction product(s) (S, \( \text{Na}_2\text{S}_2 \)) or of \( \text{Na}_2\text{SO}_4 \) (which may result from oxygen diffusion through the porous graphite rods) on the sample surface. Even during cycling, reaction
### TABLE II

**SUMMARY OF TREATMENTS AND POST-TESTS FOR CHROMIUM OXIDE BARS EXPOSED TO THE SULFUR/POLYSULFIDE MELT**

Key to treatments:  
A - initial resistivity of air annealed samples, 1500°C, 6 h  
B - held in air, 350°C for 20 h  
C - held in Na₂S₅, 350°C, no current  
D - polarized in polysulfide melt at 350°C  
E - held above Na₂S₅, 350°C, with current  
F - held above Cu/Cu₂O at 350°C

| #  | Treatment | Time (day) | Resistivity at 350°C (Ωcm) | \( E_a(D) \) (100 to 350°C) eV | \( E_a(H) \) (300 to 350°C) eV |
|----|-----------|------------|---------------------------|-----------------------------|-----------------------------|
| 1  | A         | 0          | 4.1                       | 0.36                        | 0.32                        |
| 2  | A         | 0          | 3.1(4.0)                  | 0.45                        | 0.35                        |
| 3  | A + B     | 20         | 4.4(4.5)                  | 0.35                        | 0.33                        |
| 4  | A + D     | 183        | 47.                      | --                          | --                          |
| 5  | A + D     | 183        | 47.                      | 0.41                        | 0.38                        |
|    | followed by |           |                           |                             |                             |
| 6  | A         | --         | 1.4                       | 0.33                        | 0.27                        |
| 7  | A + F     | 20         | 8.9                       | 0.37                        | 0.37                        |
| 8  | A         | 0          | 4.3                       | 0.36                        | 0.31                        |
| 9  | A         | 0          | 14.2                      | 0.42                        | 0.41                        |
| 10 | A + C     | 90         | 86(97)                    | 0.46                        | 0.33                        |
|    | followed by |           |                           |                             |                             |
| 11 | A         | --         | 1.74                      | 0.53                        | 0.29                        |
| 12 | A + D     | 210        | 510.                      | 0.57                        | 0.51                        |
| 13 | A         | 0          | 2.9                       | 0.32                        | 0.32                        |
| 14 | A + D     | 159        | 163.                      | 0.45                        | 0.37                        |
| 15 | A + E     | 159        | 90.                       | 0.65                        | 0.37                        |
| 16 | A         | 0          | 2.5                       | 0.41                        | 0.35                        |
| 17 | A + D     | 19         | 170.                      | 0.49                        | 0.47                        |
|    | followed by |           |                           |                             |                             |
| 18 | A         | --         | 3.6                       | 0.34                        | 0.36                        |

a) (Actual value) at 350°C differed more than 10% from least squared error fitted value.  
b) In situ measurement.

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products are not always totally removed by the opposite half-cycle.

3) In some cases there is evidence which implies a change in surface adsorptivity toward more preferential wetting by sulfur. But it may also be argued that the accumulation of sulfur growing with each cycle during the later stages of testing is caused by the higher current density arising from the phenomena described under 1) and 2).

There is no easy way of separating these effects, which will be of minor importance in the practical Na/S cell, where the reaction predominantly proceeds on the graphite felt rather than on the current collector.

IX. Conclusions

1) The Cr$_2$O$_3$ based materials did not exhibit morphological or chemical surface changes upon prolonged exposure to sodium polysulfide (PS) melt under dynamic conditions.

2) Wettability changes toward preferential wetting by sulfur may occur at the surface of these materials. However, the evidence is not conclusive.

3) The attainment of high densities for the sintering conditions used here depends on the addition of dopants. Dopants of 1+ and 2+ valence are effective in lowering the resistivity of high purity Cr$_2$O$_3$.

4) A high purity of the precursor oxide does not appear to be necessary for either the low resistivity (except in the case Li$_2$O), nor for high corrosion resistance in sodium pentasulfide at 350°C.

5) Bulk resistivity increases during exposure to PS melt of up to 210 days are observed for all samples. This increase is not linked to the leaching of the substituent, but rather to the equilibration with the low oxygen pressure in the polysulfide melt.

6) Among chromium oxide based materials, the high purity Cr$_2$O$_3$ doped with 0.5 mol% Li$_2$O seems most suitable as a potential coating. After the initial increase (over 30 days) the resistivity of the sample cycled in the PS melt remains constant at ~50 $\Omega$cm for 150 days. In the case of MgO doped Cr$_2$O$_3$ the value is ~100 $\Omega$cm after 100 days.
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