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EFFECTS OF SEVERAL TRACE CONTAMINANTS ON
FUEL CELL PERFORMANCE

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By

Su-Moon Park and Thomas J. O'Brien

August 1980

UNITED STATES DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
Morgantown, West Virginia

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Su-Moon Park¹ and Thomas J. O'Brien²

ABSTRACT

The electrochemical reactivity of various trace contaminants in coal gas, i.e., Hg/HgS, PbS, CdS, Sn/SnCl₂/SnCl₄, and TiO₂, in coal gas at the nickel anode and the nickel oxide cathode in a molten carbonate fuel cell have been examined thermodynamically. Calculations indicate that only SnCl₄ would undergo reduction at the cathode to SnCl₂. Other species would remain intact. Contaminants such as H₂S/SO₂ and HCl have also been included in the calculation. The results are consistent with the limited observations. Possible chemical interactions between contaminants and electrodes or electrolytes have been examined. Reactions of Sn²⁺, HgS, H₂S, and HCl with the nickel anode have negative free energies. Mercury would interact physically with the anode by forming an alloy. Reactions of Sn, SnCl₂, H₂S, and HCl with the nickel oxide cathode also have negative free energies. Reactions of Sn²⁺, HCl, H₂S, and SO₂ with carbonates have large negative free energies. Born's model of ion transfer was used to calculate the free energy change for the transfer of ions from aqueous solution to the molten carbonate solution.

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EFFECTS OF SEVERAL TRACE CONTAMINANTS ON

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Introduction

The concept of molten carbonate fuel cells is currently under development for more efficient and cleaner conversion of coal energy into electrical energy. The electrochemistry and the chemistry involved in the operation of fuel cells are described in recent reports^{1,2}. Coal gas, used as a fuel for the fuel cell, contains various contaminants in addition to the major components, carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), and water^{3,4}. These contaminants are expected to affect fuel cell performance because of their interactions with the electrodes and the electrolyte. In molten salt fuel cells, the electrolyte is usually either an equimolar mixture of lithium carbonate (Li₂CO₃) and potassium carbonate (K₂CO₃) or a mixture of 62 mole percent Li₂CO₃ and 38 mole percent K₂CO₃. Porous metallic nickel is used as the anode; porous nickel oxide as the cathode. The cell is usually operated between 900 K and 1100 K.

Experimental studies on the effects of high level contaminants such as H₂S/SO₂ and HCl on fuel cell performance have been carried out⁵. Possible adverse effects of trace contaminants have been discussed from a simple thermodynamic point of view⁶. The important point missing in that study was the consideration that the fuel cell is an electrochemical device. Due to the electrochemical nature of the fuel cell, a contaminant carried to the anode or the cathode by the fuel gas may transform into another species. The identity of contaminants

is important, since the chemistry involved in both chemical and physical interactions depends on the identity of the compound. Thus, it is very important to know the form of the contaminant and its electrochemistry at the electrode. In this report we attempt first to determine whether or not the contaminant will be electroactive and then to predict possible effects on electrolytes and electrode materials. We have selected several trace contaminants for this study. The criteria for their selection are:

1. The contaminant is consistently detected in the coal gas from various processes, and
2. the contaminant is suspected of being detrimental to fuel cell performance.

Of approximately 20 elements⁴ which are consistently detected in coal gas, only five have been selected for this preliminary study. They are cadmium, lead, titanium, mercury, and tin; their thermodynamically stable forms in the effluent stream of gasifiers are CdS, PbS, TiO₂, Hg/HgS, and Sn/SnCl₂/SnCl₄, respectively⁴. Any of these compounds would make the electrode an insulator or a semiconductor, if adsorbed at the electrode surface. Also, the reduced form of any of these metals would degrade the performance of the electrodes for the oxidation of fuels (H₂ and CO) and for the reduction of the oxidant (O₂). This is because these metals have a higher activation barrier than Ni or NiO for various electrode reactions, not because they are poor conductors.

The electrochemical behavior of a compound may be predicted if its standard electrode potential is known. That is, one can determine by comparing electrode potentials if a given compound would be electroactive in a given range

of the potential. Standard electrode potentials can be calculated, if free energies of formation of reactants and products are available^{7,8}. Since these quantities are not available for molten carbonate solutions, we have calculated them employing Born's equation⁹⁻¹². In order to employ Born's model for the ion transfer from one medium to another, we used electrochemical data reported for an equimolar mixture of lithium and sodium carbonates at 550°C (823 K)¹³. Therefore, the discussion in this report pertains to this medium, which is not the usual electrolyte for molten carbonate fuel cells. However, this is the only medium for which data are available. Free energies of formation of non-ionic compounds were taken from the JANAF table¹⁴, listed at 800 K.

Methods of Calculation

The standard electrode potential is easily calculated, provided thermodynamic data are available^{7,8}. For an electrode reaction,

the standard electrode potential, E° , is calculated from the equation,

$$\Delta G^\circ = - nFE^\circ. \quad (2)$$

Here, ΔG° , n , F , and E° are the change in standard free energy for reaction (1), the number of electrons transferred, the Faraday constant, and the standard electrode potential, respectively. Since free energies of formation (ΔG_f°) listed in the literature are measured in their standard state (e.g., 1.0 M in

the aqueous solution), Born's equation was used to calculate the free energy change as a result of transferring an ionic species from an aqueous medium to a molten salt. Born's equation has the form,⁹⁻¹²

$$\Delta G_{t\pm} = - \frac{Ne^2}{2} \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right) \frac{Z_{\pm}^2}{r_{\pm}} \quad (3)$$

where ΔG_t , N , e , ϵ , Z , and r are the free energy change for transferring an ion from water (1) to molten salt (2), Avogadro's number, the electronic charge, the dielectric constant of each medium, the charge of the cation or anion, and the radius of the ion being transferred, respectively. Although equation (3) was originally formulated for neutral ionic molecules, we have used it for calculating the standard free energies of formation of a cation or an anion. The dielectric constant of water was taken as 81. For the calculation of the dielectric constant of the molten salt, the standard electrode potentials reported for Co(II)/Co(0) and Ni(II)/Ni(0) pairs in the equimolar mixture of Li_2CO_3 - Na_2CO_3 at 550°C were used¹³. The dielectric constant of this medium was estimated to be 59.1 using electrochemical data in aqueous and in molten salts to calculate ΔG_t and then eq. (3) to determine ϵ_2 . This value was used throughout this report. Ionic radii were taken from a recent text¹⁵. For cations, the radius appropriate to a coordination number of 6 was used, except for the hydrogen ion and silver ion. For these ions, coordination numbers of 2 and 4 were assumed.

RESULTS

Standard free energies of formation (ΔG_f°)¹⁶, free energies required for the ion transfer calculated from Born's model, and calculated free energies of formation in molten salts are listed in Table 1. The ion-transfer free energy thus calculated ranged from 1 to 35 kcal/mole depending on the charge and the radius of the ion. The ΔG_f° values at 800 K for compounds other than ionic salts were taken from the JANAF table¹⁶. They are listed in Table 2. Some values were estimated using available C_p values. In this estimation, C_p and ΔS° values at 298 K were used instead of those at 800 K.

In order to evaluate this calculational method, the calculated and measured electrode potentials for a few electrode reactions studied in the same fused salt solution are compared in Table 3. The agreement between the calculated and the measured values is very good; errors are smaller than ± 50 mV. As mentioned, the ΔG_f° value for Ag_2SO_4 was estimated using C_p and ΔS° values at 298 K. Since both the heat capacity and the entropy are temperature dependent, the ΔG_f° value estimated using these quantities could have a large error. This may explain the negative deviation of the calculated electrode potential from the measured one for the $\text{Ag}_2\text{SO}_4/\text{Ag}$ pair, while the other electrode reactions have positive errors. For the H^+/H_2 -pair, the use of the ionic radius corresponding to a coordination number of 2 shows better agreement with measurements than does the choice of 1. This may indicate that hydrogen bonding is important both in the aqueous and the nonaqueous solution.

Using the ΔG_f° values in Tables 1 and 2, standard electrode potentials for anodic and cathodic reactions for trace contaminants in molten salts were calculated. The results are listed in Tables 4 and 5. The accuracy of the calculated data should be reasonably good except for reactions containing CdS and HgS. The ΔG° value for HgS was estimated using C_p and ΔS° values at 298 K, as mentioned above. For CdS, no temperature correction was made; the ΔG_f° value at 298 K was used.

The oxidation at the anode of the hydrogen and carbon monoxide in the fuel gas to H_2O and CO_2 occurs at -0.401V and -0.514V versus NHE (Table 3), respectively. Thus, the anode potential would be approximately -0.40V, if the cell operated at its open circuit potential. The cell, however, requires a high activation overvoltage, when the load is drawing 200 ~ 300 mA/cm² of current from the cell¹⁷. The actual anode potential under these operating conditions could then be as high as -0.20 ~ -0.30V. Any compound, the oxidation potential of which is lower than -0.20 ~ -0.30V, would be oxidized along with the H_2 and CO, when present in the fuel. Inspection of Table 4 reveals that none of the contaminant metallic compounds entering would be oxidized at the anode. The sulfur and chlorine compounds, whose effects on fuel cell performances have been studied⁵, are also listed in the table. Potentials for the H_2S to SO_4^{2-} reaction (Table 4) indicate that these would be oxidized at the anode to sulfate. The hydrochloric acid would be unchanged. The oxidation of H_2S to SO_4^{2-} would require some threshold concentration. This is in qualitative agreement with the experimental observations at GE⁵. They detected sulfur compounds in the form of the sulfate, but they found from a material balance that a large amount of sulfur was lost. Probably, some of the H_2S escaped with the effluent gas before it reached its

threshold concentration. It is not presently possible to calculate this threshold concentration, since no data concerning the actual anode potential versus a known reference electrode is available.

At the cathode, of various trace contaminants carried by the oxidant gas, only Sn(IV) would be reduced to Sn(II). The cathode potential for the reduction of O_2 is 0.579V versus NHE (Table 3), when the cell is operated at its open circuit potential. The actual potential could be as low as 0.4 ~ 0.5V versus NHE depending on the current density. Thus, any compound whose reduction potential is higher than 0.4 ~ 0.5V would be reduced along with the oxidant, O_2 . Only the potential for the Sn(IV)/Sn(II) pair satisfies this condition (Table 5).

In summary, only the reduction of Sn(IV) to Sn(II) at the cathode is predicted thermodynamically. Others would remain in their original form. Sulfur compounds, when introduced in the form of H_2S , SO_2 , or elemental sulfur vapor, would be oxidized to sulfate at the anode, while hydrochloric acid would not be affected. Thus, Sn(II) would be dissolved and accumulated in the electrolyte solution. Other contaminants, i.e., Sn, Hg, CdS, HgS, and PbS would accumulate in the electrolyte or as a separate phase after saturation, if there were no other interactions with electrolytes or electrodes.

Possible interactions could be through the formation of chemical bonds and/or physical adsorption at the electrode surface. Whether or not a proposed chemical reaction could occur can be determined by calculating the free energy change for the reaction. Physical interactions may also be evaluated in the same manner, provided pertinent data are available. Due to the lack of such data, we will

not address this type of interactions. In this report we will only consider the chemical interaction of trace contaminants with the electrolyte or the electrodes.

The most straightforward reaction with the electrolyte or electrodes among various contaminants would be that of Sn(II); Sn(II) will be dissolved in the electrolyte. Other contaminants such as HgS, PbS, and CdS would dissolve until the solution is saturated. Then they would start to form a separate phase. Solubilities of these compounds in molten salts would be higher than in the aqueous solution, but they would still be sparingly soluble salts. Elemental contaminants, i.e., Hg and Sn, would accumulate in the cell as sludge-like material, only if they escape from the electrode.

For chemical interactions, two types of chemical reaction may be considered, electron transfer or simple replacement. We will consider reaction of these contaminants with the Ni anode first, and then reactions with the NiO cathode. The electrolyte will be considered later. Possible electron transfer reactions of trace contaminants with the anode, along with their free energy of reaction, are:

We can see that reactions (4), (7), (9), and (10) are thermodynamically favorable. The results of these reactions would be the deposition of the metallic tin (reaction [4]), coating the electrode surface with sulfides (reactions [7] and [9]), or the dissolution of the anode into the solution (reaction [10]). While all these reactions would be detrimental to the electrode operation, reaction (7) seems particularly deleterious to the electrode surface. As pointed out in the Introduction, reactions (4), (7), and (9) would reduce the electrode activity (1) by blocking the approach of H₂-molecules to the anode (catalyst poisoning) through formation of thin films, (2) by making the electrode either a semiconductor or an insulator (NiS films), and (3) by raising an activation barrier for an electrode reaction (Sn and Hg films). The NiS film will increase the ohmic loss, whether it is a semiconductor or an insulator. The formation of tin films will lower the exchange current density for the hydrogen oxidation by at least four orders of magnitude; the mercury film will lower the oxidation efficiency by about seven orders of magnitude¹⁸.

Elemental contaminants, Sn and Hg, can undergo electron transfer type reactions with the cathode as follows:

Of these two reaction, only reaction (12) appears to be important, if there are not any physical interactions. The effect of the resulting SnO_2 film (reaction [12]) is not known. When heavily doped, n- SnO_2 is a good semiconductor with a high oxygen overpotential¹⁹. Also, since the nickel oxide is of a p-type²⁰ and SnO_2 is of an n-type, a power loss due to the p-n junction formation is possible.

At the cathode, simple exchange reactions, where negatively charged atoms are exchanged, appear to be more important. These reactions include:

As can be seen from free energy values, the last three reactions are important. Again, these reactions will cause either the dissolution of the electrode material (reactions [16] and [18]) or the formation of the NiS film on the cathode (reaction [17]). The reaction with TiO_2 has not been considered, since the only effect would be the exchange of oxygen atoms.

The free energy analysis described above indicates that neither PbS nor CdS would interact chemically with the anode or the cathode. This material would probably accumulate in the electrolyte, degrading its quality. It may also plug electrode pores, reducing the activity of the electrodes.

Physical interactions through adsorption processes at the electrode surface could be as important as chemical interactions, but currently it is difficult to estimate their importance. Physical interactions are extremely important in the case of Hg, which forms an amalgam with metals. For the adsorption of Hg by the nickel anode, i.e.,

the ΔG° value was estimated⁶ to be -38 kcal/mole at 900 K. This number indicates that the adsorption process of Hg at the Ni-surface is essentially encounter-controlled. A similar calculation cannot be made for Sn, HgS, PbS, CdS, and TiO_2 due to the lack of thermodynamic data. As pointed out already, the coverage of the electrode surface with any of these compounds, especially with Hg, is detrimental to the fuel cell operation¹⁸. Effects of these contaminants on fuel cell performances may only be determined experimentally.

Finally, possible reactions of the contaminants with the electrolyte are listed, along with their free energy changes:

As before, a similar reaction with TiO_2 is not possible. Also, no reactions of alkali cations with the contaminants were considered. Of the reactions listed above, reactions (23), (24), and (26) are important. As can be seen the effect of these reactions on the electrolyte would be the loss of electrolyte and the introduction of a new ionic species (SO_4^{2-}) or a new phase (SnO_2). This could change physical properties such as viscosity and conductivity, as already pointed out.

Summary and Discussion

The electrochemical reactivity of various trace contaminants in fuel gas at the nickel anode and the nickel oxide cathode in a molten carbonate fuel cell have been examined thermodynamically. Calculations indicate that only SnCl_4

would undergo reduction at the cathode to SnCl_2 . Other species would remain intact. Contaminants such as $\text{H}_2\text{S}/\text{SO}_2$ and HCl have also been included in the calculation. The results are consistent with the observed phenomenon. Possible chemical interactions between contaminants and electrodes or electrolytes have been examined. The results indicate that reactions of Sn^{2+} , HgS , H_2S , and HCl with the nickel anode have negative free energies. Mercury would interact physically with the anode by forming an alloy. Reactions of Sn , SnCl_2 , H_2S , and HCl with the nickel oxide cathode also have negative free energies. Reactions of Sn^{2+} , HCl , H_2S , and SO_2 with carbonates have large negative free energies.

Born's model of ion-transfer was used to calculate the free energy change for the transfer of ions from aqueous solution to the molten carbonate solution. The use of Born's equation for the estimation of the free energy of the ion-transfer assumes the dielectric continuum model for the solvation of the cation. The agreement between the calculated and measured data appears reasonable for the limited amount of data available. However, this does not adequately prove that this model describes the change in solvation energy between two different solvents. More experimental data are necessary to validate this model. Also, since the data used correspond to slightly different medium from the actual fuel cell electrolyte, the results only approximate the operating conditions of a fuel cell. Data are needed in the proper molten salt mixture at the proper temperature.

The dielectric constant, estimated from the data for the equimolar mixture of Li_2CO_3 - Na_2CO_3 using Born's equation, was 59.1, indicating that this solvent would be poorer than water for ionic species. While this number appears reasonable, it is much larger than the early estimation²¹ of 3 ~ 5. Whether or not there has been a gross error in this calculation remains to be answered by more experimental results. The agreement is good, as pointed out, but it could be fortuitous. It is important to remember that the solvation structure of cations was assumed to be essentially the same in both media. This means that the hydrated cation in aqueous solution only replaces water molecules with carbonate molecules upon transferring.

In calculating free energies for reactions involving compounds such as CdS , HgS , PbS , and TiO_2 , we have treated them as a solid phase. Since we are moving these species from a more polar solvent, H_2O ($\epsilon = 81$), to a less polar medium, molten carbonate ($\epsilon = 59$), they would be expected to be less soluble. Conversely, the solubility would increase due to the increase in temperature. As an example, the solubility product constant for the process,

is calculated to be 4.1×10^{-13} in the molten salt at 800 K, compared with 8.8×10^{-29} in water at 298 K. The increase in the solubility is largely attributed to the higher temperature. Although we believe that these calculations are reasonably accurate, they point out the necessity of measuring fundamental thermodynamic quantities.

Recommendations

1. Thermodynamic properties of molten carbonate solutions at the operating temperature of fuel cells must be measured and compiled. This can be accomplished by solubility measurements of sparingly soluble salts and by electrochemical potential measurements of various half-cell reactions.
2. A better model, to describe the molten salts as a solvent system, must be developed to employ in compiling the data. The model should be capable of describing solvation energies as well as structure.
3. Effects of trace contaminants on fuel cell performance must be studied experimentally by both electrochemical and surface spectroscopic techniques. The results can then be compared with theoretical predictions obtained from the model.
4. These studies must be expanded to include all the contaminant elements that are usually detected in the coal gas.

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References

1. IGT Fuel Cell Handbook, to be published.
2. K. Kinoshita, "Critical Survey on Electode Aging in Molten Carbonate Fuel Cells," Argonne National Laboratory, Argon, IL, 1979.
3. J. H. Kuhn, F. Fiene, and R. Harvey, "Geochemical Evaluation and Characterization of a Pittsburgh No. 8 and A Rosebud Seam Coal," Illinois State Geological Survey, Urbana, IL, 1978.
4. "Coal Derived Fuel Gases for Molten Carbonate Fuel Cells," TRW Energy Systems Planning Division, Morgantown Energy Technology Center, Morgantown, WV, 1979.
5. "Development of Molten Carbonate Fuel Cells for Power Generation," General Electric Company Corporate Research and Development, Schenectady, NY, 1979.
6. D. Bloomfield, A. Gelb, S. Guberman, and P. Lewis, "Interaction of Trace Species with the molten Carbonate Fuel Cell," Physical Sciences, Inc., Woburn, MA, 1979.
7. M. Pourbaix, "Atlas of Electrochemical Equilibria," Pergamon Press, London, 1966.
8. M. Pourbaix, "Lectures on Electrochemical Corrosion," Plenum Press, NY, 1973.

9. M. Born, Z. Phys, 1, 45 (1920).
10. J. Bronsted, Chem. Rev., 5, 231 (1928).
11. J. F. Coetzee and J. J. Campion, J. Am. Chem. Soc., 89, 2513 (1967).
12. S. Goldman and R. G. Bates, ibid., 94, 1476 (1972).
13. J. A. Plambeck, "Fused Salt Systems," in "Encyclopedia of Electrochemistry of the Elements," A. J. Bard Ed., Volume X, Marcel Dekker, Inc., New York, NY, 1976, Chapter 15.
14. D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd Ed., NSRDS-NBS 37, U.S. Government Printing Office, Washington, D.C., 1971.
15. J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper and Row Publishers, NY, 1972.
16. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schum, "Selected Values of Chemical Thermodynamic Properties," NBS TN 270-3, 270-4, 270-6, U.S. Government Printing Office, Washington, D.C., 1968, 1969, and 1971, respectively.
17. H. A. Laitinen and W. E. Harris, "Chemical Analysis," 2nd Ed., McGraw-Hill Book Co., Inc., NY, 1974.

18. S. Srinivasan, H. Wroblowa, and J. O'M. Bockris, in "Advances in Catalysis and Related Subjects," D. D. Eley, H. Pines, and P. B. Weisz, eds., Volume 17, Academic Press, New York, NY, 1967.
19. A. K. Vijh, "Electrochemistry of Metals and Semiconductors," Marcel Dekker, Inc., New York, NY, 1973.
20. D. Yohe, A. Riga, R. Greef, and E. Yeager, Electrochim. Acta, 13, 1351 (1968).
21. G. J. Janz, "Molten Salts Handbook," Academic Press, New York, NY, 1967, page 356.

TABLE 1
Free Energies of Various Ions
kcal/mole

Ions	ΔG_f° (Aq. Soln.)	ΔG_t	ΔG_f° (Molten Salt) ^a
Sn^{2+}	-6.457	4.97	1.48
Sn^{4+}	0.60	35.18	35.78
Cd^{2+}	-18.542	6.39	-12.15
Hg_2^{2+b}	36.70	3.13	39.83
Hg^{2+}	39.30	5.95	45.25
Pb^{2+}	-5.83	5.17	-0.66
K^+	-67.451	1.10	-66.35
H^+	0.00	-8.43	-8.43
Cl^-	-31.372	0.84	-30.53
S^{2-}	20.5	3.30	23.8
SO_3^{2-c}	-116.3	2.6	-113.7
SO_4^{2-}	-177.97	2.64	-175.33
CO_3^{2-}	-126.17	3.28	-122.89

a. Equimolar mixture of Li_2CO_3 and Na_2CO_3 at 823 K.

b. An ionic radius twice that of Hg^+ was assumed.

c. The same ionic radius as that of SO_4^{2-} was assumed.

TABLE 2

Free Energies of
Formation at 800 K^a

Compounds	ΔG_f° , kcal/mole ^b
H ₂ O(g)	-48.646
CO ₂ (g)	-94.556
S(g)	40.171
H ₂ S(g)	-12.183
SO ₂ (g)	-72.574
CO(g)	-43.612
HCl(g)	-23.774
CdS(s)	-37.4 ^c
HgS(s)	-1.2 ^d
Pbs(s)	-22.202
TiO ₂ (s)	-189.311
Ag ₂ SO ₄ (s)	-127.9 ^d
NiS(s)	-19.706
CdO(s)	-35.5 ^d
NiO(s)	-34.0
PbO(s)	-33.281
HgU(s)	2.347
NiCl ₂ (l)	-58.9 ^e
SnO(s)	-44.5
SnCl ₂ (l)	-60.5 ^e
SnO ₂ (s)	-93.3 ^d

- a. The state of compounds is indicated in parenthesis.
- b. All data are taken from the JANAF tables¹⁴, unless otherwise indicated.
- c. Taken from NBS Technical Note 270-3. Value at 298 K.
- d. Estimated from the C_p value given in NBS Technical Notes.
- e. Estimated from the electrode potential of $\text{Ni}^{2+}/\text{Ni(O)}$ pair and corrected ΔG_f° of Cl^- in melts (Table 1).

TABLE 3

Comparisons of Calculated and Measured
Electrode Potentials
Equimolar $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ at 550°C

Reactions	E°-Values, V vs. NHE		Error, mV
	Calculated	Measured ^a	
$2\text{H}^+(\ell) + 2e = \text{H}_2(\text{g})$	-0.365	-0.401	36
$2\text{CO}_2(\text{g}) + \text{O}_2(\text{g}) + 4e = 2\text{CO}_3^{2-}(\ell)$	0.614	0.579	35
$2\text{CO}_2(\text{g}) + 2e = \text{CO}(\text{g}) + \text{CO}_3^{2-}(\ell)$	-0.490	-0.514	24
$\text{Ag}_2\text{SO}_4(\text{s}) + 2e = 2\text{Ag}(\text{s}) + \text{SO}_4^{2-}(\ell)$	1.029	1.049	-20

a. Ref. 13.

TABLE 4

Calculated Electrode Potentials in Molten Salts
Anodic Reactions

Elements	Reactions	E°, V vs. NHE
Tin	$\text{Sn}^{2+} + 2e = \text{Sn(s)}$	-0.032
	$\text{Sn}^{4+} + 4e = \text{Sn(s)}$	0.389
	$\text{Sn}^{4+} + 2e = \text{Sn}^{2+}$	0.808
	$\text{Sn}^{4+} + \text{Cl}_2(\text{g}) + 4e = \text{SnCl}_2(\text{l})$	1.066
Cadmium	$\text{Cd}^{2+} + \text{S}(\text{g}) + 2e = \text{CdS(s)}$	1.418
	$\text{Cd}^{2+} + \text{SO}_3^{2-} + 6\text{H}^+ + 6e = \text{CdS(s)} + 3\text{H}_2\text{O(g)}$	0.050
	$\text{Cd}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8e = \text{CdS(s)} + 4\text{H}_2\text{O(g)}$	-0.124
Mercury	$\text{Hg}^{2+} + 2e = \text{Hg(g)}$	1.055
	$\text{Hg}^{2+} + 2e = 2\text{Hg(g)}$	0.864
	$\text{Hg}^{2+} + \text{S}(\text{g}) + 2e = \text{HgS(s)}$	1.878
	$\text{Hg}^{2+} + \text{SO}_3^{2-} + 6\text{H}^+ + 6e = \text{HgS(s)} + 3\text{H}_2\text{O(g)}$	0.203
	$\text{Hg}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8e = \text{HgS(s)} + 4\text{H}_2\text{O(g)}$	-0.009
Lead	$\text{Pb}^{2+} + \text{S}(\text{g}) + 2e = \text{PbS(s)}$	1.294
	$\text{Pb}^{2+} + \text{SO}_3^{2-} + 6\text{H}^+ + 6e = \text{PbS(s)} + 3\text{H}_2\text{O(g)}$	0.023
	$\text{Pb}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8e = \text{PbS(s)} + 4\text{H}_2\text{O(g)}$	-0.144
Sulfur	$\text{S}(\text{g}) + 2\text{H}^+ + 2e = \text{H}_2\text{S(g)}$	0.770
	$\text{SO}_3^{2-} + 8\text{H}^+ + 6e = \text{H}_2\text{S(g)} + 3\text{H}_2\text{O(g)}$	-0.166
	$\text{SO}_4^{2-} + 10\text{H}^+ + 8e = \text{H}_2\text{S(g)} + 4\text{H}_2\text{O(g)}$	-0.286
	$\text{SO}_4^{2-} + 4\text{H}^+ + 2e = \text{SO}_2(\text{g}) + 2\text{H}_2\text{O(g)}$	-0.907
	$\text{SO}_3^{2-} + 6\text{H}^+ + 4e = \text{S(g)} + 3\text{H}_2\text{O(g)}$	-0.817
	$\text{SO}_4^{2-} + 8\text{H}^+ + 6e = \text{S(g)} + 4\text{H}_2\text{O(g)}$	-0.639
	$\text{SO}_4^{2-} + 2\text{H}^+ + 2e = \text{SO}_3^{2-} + \text{H}_2\text{O(g)}$	-0.647
Chlorine	$\text{Cl}_2(\text{g}) + 2e = 2\text{Cl}^-$	1.324
Titanium	No further oxidation of TiO_2 .	--

TABLE 5

Calculated Electrode Potentials in Molten
Salts -- Cathodic Reactions

Elements	Reactions	E°, V vs. NHE
Tin	$\text{Sn}^{2+} + 2e = \text{Sn(s)}$	-0.032
	$\text{Sn}^{4+} + 4e = \text{Sn(s)}$	0.388
	$\text{Sn}^{4+} + 2e = \text{Sn}^{2+}$	0.808
Cadmium	$\text{CdS(s)} + 2e = \text{Cd(s)} + \text{S}^{2-}$	-1.327
Mercury	$\text{HgS(s)} + 2e = \text{Hg(l)} + \text{S}^{2-}$	-0.653
Lead	$\text{PbS(s)} + 2e = \text{Pb(s)} + \text{S}^{2-}$	-0.997
Titanium	$\text{TiO}_2(\text{s}) + 4\text{H}^+ + 4e = \text{Ti(s)} + 2\text{H}_2\text{O(g)}$	