Electrochemical Studies of Molten Sodium Carbonate

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Electrochemical studies of sparged beds of sodium carbonate at 900 °C employing mixtures of oxygen, carbon dioxide, and water vapor were conducted to determine the identities and relative concentrations of melt species. Analysis of experimental current–potential curves was done by fitting the curves with composite curves that consisted of the algebraic sum of eight computer-generated theoretical waves. The most prominent features of the curves were the 1-electron reversible couple O_2^-/O_2^{2-} superimposed on a 2-electron reversible couple proposed to be CO_4^{2-}/CO_3^{2-}, O^{2-} and, at higher overpotential, a 2-electron irreversible wave proposed to be the reduction of $C_2O_6^{2-}$ ion. ESR spectra confirmed the presence of superoxide ion in frozen-melt matrix. Under sparged conditions, the thermal decomposition of sodium carbonate appears to produce peroxide ion in addition to oxide ion. A sequence of reactions is proposed to account for the interconversion of melt species.

Introduction

Alkali-metal carbonates have been shown to be effective catalysts for the gasification of carbonaceous materials (including coal)[1] and the destruction of toxic chemical wastes.[2] They also provide the basis for the molten carbonate fuel cell.[3] The optimization of the processes involved requires a fundamental understanding of the composition of molten carbonates and how the composition changes with changes in the supernatant atmosphere. Toward that end, several studies employing electrochemical techniques have been conducted.[4–12] With the exception of two studies in which lithium carbonate was used,[7,9] all were conducted in eutectic mixtures of Li/Na/K,[4,5,7,8,11] Li/Na,[6] Na/K,[8,10] and Li/K[12] carbonates.

As part of an overall study directed toward understanding the mechanism of carbon oxidation in molten-salt media,[13–15] the present research was undertaken to determine the identities and relative concentrations of the species that exist in molten sodium carbonate under various experimental conditions.

Techniques capable of monitoring melt composition include removal and chemical analysis of melt samples, spectroscopic measurements (Raman and infrared), and electrochemical measurements. It was found that removal of melt samples by insertion of a "cold" rod into the melt did not provide representative samples. Fractional crystallization occurred with the highest melting species preferentially freezing on the rod. This technique also had the disadvantages of being slow and increasing the possibility of melt contamination. Spectroscopic procedures were not attempted because of difficulties anticipated in the construction of apparatus required to make in situ measurements at the high temperatures employed. These factors led to the choice of electrochemical measurements to determine the melt composition even though ambiguities often exist in the interpretation of electrochemical results. Attempts to construct a rotating-disk electrode for use in the aggressive environment of sodium carbonate at 900 °C were unsuccessful largely due to the invasion of melt between the gold-disk electrode surface and the alumina tube in which the disk was mounted. Therefore, it was necessary to employ a stationary gold working electrode.

During the course of conducting exploratory single-sweep current–potential scans of molten sodium carbonate in pseudo steady state with various sparge gas compositions (carbon dioxide, oxygen, and nitrogen), evidence for the existence of at least eight electrochemical waves was observed in separate experiments (five cathodic and three anodic including the cutoff waves). Because of the complexity of the observed current–potential curves that consist of these eight overlapping waves, analysis by simple peak-current and peak-potential measurements was found to be inadequate. Instead, composite curves made up of the algebraic sum of eight computer-generated theoretical waves were fitted to the experimental curves by using a nonlinear least-squares procedure. The theoretical waves were generated by using current and potential functions for charge transfers at stationary electrodes developed by Nicholson and Shain.[16]

Experimental Section

Materials. Air ("breathing air": 20.9% oxygen, 0.03% carbon dioxide, and 78.1% nitrogen), oxygen (99.993%), carbon dioxide (99.99%), nitrogen (99.999%), and calibration gas mixtures were obtained from and analyzed by Airco.

Sodium carbonate (Baker anhydrous reagent grade, 99.5%) contained nitrogen compounds (N, 0.001%), phosphorus (PO_4, 0.001%), silica (SiO_2, 0.005%), sulfur (SO_4, 0.003%), and iron (Fe, 5 ppm).

Sodium oxide (Na_2O, 98%) and sodium superoxide (NaO_2, 90%) were obtained from Alfa Products. Sodium peroxide (Na_2O_2, 93%) was obtained from Mallinckrodt.

All parts of the apparatus contacting the molten sodium carbonate were constructed of fine gold or 99.8% alumina (Coors AD-998).

Apparatus. The apparatus, shown schematically in Figure 1, consisted of an electrochemical cell contained in a tube furnace. Sparge gas mixtures (oxygen, carbon dioxide, and nitrogen) were prepared with a gas blender (Medicor, Inc., Model PGM-3) and were passed through the melt by using a peristaltic type pump (Masterflex, Cole-Parmer Inc.) equipped with Tygon tube. Part of the exhaust gas from the cell was pumped through an oxygen analyzer (Beckman Model 755), through carbon dioxide and carbon monoxide analyzers (Horiba Model PIR-2000), and finally through a gas chromatograph (Hewlett-Packard Model 5840A). Data from the oxygen, carbon dioxide, and carbon monoxide analyzers together with melt and furnace

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Figure 1. Schematic of the apparatus.

temperatures and time were gathered every 30 s, partially reduced, and stored on magnetic tape with use of a data acquisition system (Hewlett-Packard Model 3052A). GC data were obtained every 3.5 min and stored on tape. These data could be recalled and plotted with a Hewlett-Packard Model 9872A plotter. Electrochemical measurements were made with a Princeton Applied Research Model 170 system. Curve fitting was accomplished with use of an HP-9845-B computer. ESR measurements were done with a Bruker ER-200 spectrometer.

The electrochemical cell (Figure 2) consisted of an alumina containment vessel (8 × 46 cm) closed at one end. The open end was fitted with an epoxy seal to a water-cooled stainless-steel collar. A stainless-steel cover plate fitted with openings for the electrodes, thermowell, gas-sample tube, exhaust-gas port, and sparge tube was clamped to the collar equipped with an O-ring seal. The openings in the cover plate were equipped with stainless-steel fittings with finger-tightened O-ring seals (Cajon Co.), which provided vacuum-tight seals around the tubes and allowed vertical adjustment. A flat-bottom alumina crucible (7 × 15 cm), which contained the melt, rested on alumina sand at the bottom of the containment vessel. A series of five alumina heat shields suspended on platinum wires and held apart with alumina tube spacers were placed between the crucible and the cover plate to minimize thermal convection within the cell. The cell was mounted vertically in the center of a tube furnace (10 × 61 cm), which consisted of a single heating unit controlled by a proportional controller. A three-electrode system was used. The working electrode consisted of a rectangular gold-sheet (1 × 0.5 × 0.025 cm) spot welded to 0.05-cm (diameter) gold lead wire and allowed to extend 1 cm into the melt providing an effective geometric surface area of 1.16 cm². The counterelectrode was a gold-foil cylinder (4 × 7 cm) that rested on the bottom of the crucible and was connected by a 0.05-cm (diameter) gold lead wire. The reference electrode consisted of a 0.05-cm (diameter) gold wire that dipped into the melt within an alumina tube that rested on the bottom of the crucible. The melt within the tube was in contact with a slow stream (40 mL/min) of oxygen (33%) and carbon dioxide (67%). This reference electrode was previously described in detail.[17]

A Pyrex solids-addition device fitted with a straight-bore Teflon stopcock could be installed at the top of the sparge tube. The sparge gas flowed through a tee below the stopcock and thence down the sparge tube. A weighed sample of the solid to be added to the melt was placed in a sealed chamber above the stopcock. Turning the

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Figure 2. Schematic of the electrochemical cell (thermowell and counterelectrode omitted for clarity).

stopcock permitted the solid to drop directly down the sparge tube with the sparge gas into the melt.

Procedure. The internals of the electrochemical cell (crucible, heat shields, counterelectrode, etc.) were assembled and attached to the cover plate. The remaining electrodes, thermowell, and sparge tube were fitted through the cover plate and sealed. The crucible was charged with 175 g of sodium carbonate (~90 mL of melt) and the assembly slowly lowered (over ~6 h) into the containment vessel, which was maintained at 900 °C. When the crucible was in final position, the cover plate was secured to the containment-vessel collar with bolts. With the working electrode, reference electrode, and sparge tube above the surface of the melt, the cell was slowly evacuated by using a mechanical pump equipped with an oil diffusion pump to a final pressure, typically ~133 Pa (1 torr). The vacuum was broken with carbon dioxide; the thermowell, reference electrode, and sparge tube were lowered into the melt, and the melt was sparged with carbon dioxide for at least 2 h prior to the beginning of an experiment. During this time, the reference-electrode gas was allowed to "equilibrate" with the reference melt. This procedure was followed each time the melt was replaced; however, the melt was not changed before each experiment. Between experiments in which the melt was not replaced, the melt was sparged with carbon dioxide for an overnight period to convert "oxides" present to carbonate. The sparge-gas flow rate used in all of the experiments was 0.239 L/min (25 °C, 1 atm).

The majority of the electrochemical measurements were controlled-potential sweeps (0.5 V/s) from the rest potential (cathodically to −1.40 V and anodically to +0.10 V). Prior to the cathodic sweep, the pumps that supplied the sparge gas and extracted the analytical sample gas (exhaust) were stopped for approximately 15 s. The sweep was made, and the pumps were started and allowed to run 15 s. The pumps were again stopped for 15 s, and the anodic sweep was initiated at the rest potential. After the anodic sweep, the pumps were started and allowed to run until the next electrochemical measurement. During the course of an experiment, the composition of the exhaust gas was monitored as described above.

Results

Analysis of Experimental Curves. Cyclic triangular-sweep and single-sweep scans of molten sodium carbonate (900 °C) after air sparge for 48 h are shown in Figure 3. The cyclic

Figure 3. Current–potential curves of sodium carbonate (900 °C) after air sparge: (a) cyclic scan beginning cathodic from the rest potential and (b) single-sweep scans both cathodic and anodic from the rest potential (solid line) with the computer-generated composite curve (dashed line) and component waves indicated (dotted lines).

Table I. Potentials, Peak Currents, and Electrons Transferred for Component Waves in Sodium Carbonate Sparged with Air at 900 °C

wave	$E_{1/2}$, V	i_p, mA	n
cathodic 1	−0.467	26.41	1
cathodic 2	−0.448	7.75	2
cathodic 3	−1.003	32.76	2
cathodic 4	−1.243	7.21	2
cathodic 5[a]	−1.422	37.20	2
anodic 6	−0.350	−18.13	2
anodic 7	−0.301	−0.52	1
anodic 8[b]	0.082	−17.87	2

[a] Cathodic cutoff. [b] Anodic cutoff.

scan shows that the initial cathodic wave is reversible (cathodic peak potential $E_{p,c}$ = −0.56 V; anodic peak potential $E_{p,a}$ = −0.37 V) with n = 1.17 calculated from eq 1.[18] The second

$$E_{p,c} - E_{p,a} = -2.2RT/nF \qquad (1)$$

cathodic wave ($E_{p,c}$ = −1.06 V) is irreversible as shown by the cyclic scan and by an observed cathodic shift with increased sweep rate as predicted by theory.[16] The results of the curve-fitting procedure applied to the single-sweep scan are shown in Figure 3b. The root-mean-square difference between the experimental curve (solid line) and the computer-synthesized composite curve (dashed line) is 0.567 mA over the 1.5-V range. The eight component waves are shown (dotted lines). The respective $E_{1/2}$ (V), peak current (i_p, mA), and number of electrons transferred (n) for each wave are listed in Table I. The analysis shows that the cathodic part of the single-sweep scan of sodium carbonate melt under air sparge is composed largely of a 1-electron wave (wave 1) and a 2-electron wave (wave 3) with smaller contributions from two 2-electron waves (waves 2 and 4) (excluding the 2-electron cutoff wave, wave 5). The anodic part of the scan is composed of a 2-electron wave (wave 6) with a very small contribution from a 1-electron wave (wave 7) (excluding the 2-electron

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Figure 4. Peak currents of single-sweep scans measured in sodium carbonate (900 °C) sparged with nitrogen and exhaust-gas CO_2 concentration plotted as a function of reaction time.

cutoff wave, wave 8). It was found that all of the experimental curves obtained in this study could be fitted with the waves shown in Figure 3b with the maximum root-mean-square differences between the experimental curves and synthesized composite curves <4% of the largest wave excluding the cutoff waves).

In the following experiments, sodium carbonate melt was sparged with various gases to determine the effect of oxygen pressure, carbon dioxide pressure in the presence and absence of oxygen, and the addition of water vapor on the electroactive species.

Nitrogen Sparge. After treatment with carbon dioxide, sodium carbonate melt (900 °C) was sparged with nitrogen for 2880 min. The results are shown in Figure 4. The carbon dioxide concentration of the exhaust gas decreased from 100% to approximately 0.05% after 500 min and remained near that concentration for the remainder of the experiment. For the first 46 min, oxygen (<0.05%) was observed in the exhaust gas. Thereafter, with the exception of carbon dioxide and nitrogen, no other gaseous products were detected. In the first 400 min, the 1-electron anodic wave 7 (Figure 3b) and the 2-electron anodic wave 6 increased rapidly (from 0 to −4.79 mA and from 0 to −4.48 mA, respectively). After 400 min, both waves continued to increase but at a slower rate (to −13.68 mA for wave 7 and −9.45 mA for wave 6 after 2880 min). The remaining waves were relatively unchanged during the experiment. The rest potential at t = 0 (pure carbon dioxide sparge) was −0.150 V but shifted gradually with the increase in the anodic part of the curve to −0.652 V at the end of the experiment.

In three separate experiments, sodium carbonate melt (900 °C) was treated with carbon dioxide and sparged with nitrogen for 100 min, and then the indicated salt (sodium oxide, sodium peroxide, or sodium superoxide) was added without interruption of the nitrogen flow. The nitrogen sparge, prior to the addition of the "oxides", effectively removed the carbon dioxide from the system with minimal effect on the melt composition.

Figure 5. Cyclic scan of sodium carbonate (900 °C) under argon sparge beginning cathodic from the rest potential 78 min after the addition of sodium oxide.

The addition of sodium oxide (0.4077 g, 6.45 mmol, 98% pure) caused an immediate increase (from −4.50 to −42.33 mA) in the peak current of the 1-electron anodic wave (wave 7). The 2-electron anodic wave (wave 6) also increased but more slowly (from −3.99 to −4.12 mA). The carbon dioxide concentration of the exhaust gas decreased from approximately 0.10% to 0.05%, and no oxygen was observed. In a similar experiment employing argon sparge, a cyclic voltammogram taken 78 min after the addition of sodium oxide (0.4108 g, 6.63 mmol) showed the presence of a reversible couple ($E_{p,c}$ = −0.49 V; $E_{p,a}$ = −0.40 V) with n = 2.47 (Figure 5).

Addition of sodium peroxide (0.5215 g, 6.22 mmol, 93% pure) caused cathodic wave 1 to increase from 1.57 to 26.47 mA and then decrease to 0.04 mA within the first 7 min after the addition. Cathodic wave 2 increased from 0 to 51.44 mA, anodic wave 6 increased from −3.00 to −73.73 mA in the first 4 min, and then both waves decreased rapidly over approximately the next 30 min. Anodic wave 7 increased from −2.79 to −59.72 mA over the first 9 min and then remained relatively constant. Oxygen was evolved immediately with the addition of sodium peroxide (3.80 mmol over approximately 15 min), which suggests that peroxide ion decomposed to oxide ion and oxygen, according to eq 2. The quantities of oxygen and oxide ion expected would be 3.11 and 6.22 mmol, respectively.

$$O_2^{2-} \rightleftharpoons {}^1/_2O_2 + O^{2-} \tag{2}$$

Addition of sodium superoxide (0.2328 g, 3.81 mmol, 90% pure) caused the immediate increase of cathodic wave 1 from 1.35 to 29.64 mA followed by a rapid decrease to 3.45 mA after 13 min. Cathodic wave 2 and anodic wave 6 (2-electron waves) increased from 0.02 to 12.31 mA and from −2.54 to −39.73 mA, respectively, over the first 3 min and then decreased slowly over the next 100 min. Anodic wave 7 increased slowly over the first 23 min from −2.54 to −14.75 mA and then

decreased to −7.60 mA after 100 min. Oxygen (3.00 mmol) was evolved over the first 15 min after the addition of sodium superoxide, which suggests that superoxide ion decomposed according to eq 3 in which 2.86 mmol of oxygen and 1.91 mmol of oxide ion would be expected.

$$2O_2^- \rightleftharpoons {}^3/_2O_2 + O^{2-} \tag{3}$$

A comparison of the relative measured peak currents and calculated concentrations of the four significant species 1 min after the addition of the above salts is presented in Table II. Concentrations were calculated by using an assumed diffusion coefficient of 1×10^{-5} cm^2/s for all species to normalize the 1- and 2-electron waves. Inspection of Table II shows that, 1 min after the addition of sodium oxide to the melt, wave 7 was the dominant wave. Similarly, 1 min after addition of sodium superoxide, wave 1 was the dominant wave. Finally, 1 min after the addition of sodium peroxide to the melt, cathodic wave 1 and anodic wave 7 both increased to approximately the same concentration. Anodic wave 6 had increased only slightly in the first minute.

Nitrogen and Then Air Sparge. After treatment with carbon dioxide, sodium carbonate melt (900 °C) was sparged with nitrogen for 100 min and then sparged with air. The carbon dioxide concentration of the exhaust gas decreased over the first 100 min from 100% to ~0.09%, and oxygen was detected (<0.04%). The results of the first 400 min after the air sparge was started are shown in Figure 6.

When the air sparge was begun, the carbon dioxide concentration increased to ~0.25% and then decreased during the remainder of the experiment to a final concentration of 0.06% after 1441 min. Approximately 10 min was required for the concentration of oxygen in the exhaust gas to reach 20.9% (the approximate concentration of oxygen in air). Cathodic wave 1 increased rapidly over the first 60 min from 2.53 to 20.56 mA and then continued to increase slowly over the remainder of the experiment to 21.34 mA after 491 min and finally 29.65 mA after 1441 min. Cathodic wave 2 increased over the first 300 min and then remained relatively constant at 15.00 mA. Cathodic wave 3 and anodic wave 6 increased slowly over the course of the experiment to 27.30 and −24.76 mA, respectively, after 1441 min. The remaining electrochemical waves were relatively unchanged during the air part of the experiment.

These results show clearly that oxygen is required for the production of the species responsible for waves 1, 2, and 3 when compared to the results of the previous nitrogen-sparged experiment in which these waves were essentially absent. Moreover, anodic wave 7, which was the predominant wave in the nitrogen-sparged experiment, was absent in this air-sparged experiment. Anodic wave 6 was observed in both experiments with the highest concentration in the air-sparged experiment. Finally, this experiment shows that even after 1441 min of air sparge, the composition of the melt was still changing.

Table II. Relative Concentrations of Melt Species 1 min after Addition of Indicated Salt[a] (N₂ Sparge, 900 °C)

salt	mmol added	exhaust O₂ concn, %	wave 1 i_p[b]	wave 1 C[c]	wave 2 i_p[b]	wave 2 C[c]	wave 6 i_p[b]	wave 6 C[c]	wave 7 i_p[b]	wave 7 C[c]
Na₂O	6.45	0	0.63	0.18	4.28	0.42	−10.64	1.06	−42.33	11.89
Na₂O₂	6.22	8.82	7.51	2.11	4.15	0.41	−8.10	0.80	−9.10	2.56
NaO₂	3.81	9.07	29.64	8.32	11.28	1.12	−36.97	3.67	−2.66	0.75

[a] Calculated from eq 4,[16] where i_p = peak current (mA), n = number of electrons transferred, F = 964 89, A = area of electrode (1.16 cm²),

$$i_p = 0.446 \frac{n^{3/2}F^{3/2}AD^{1/2}v^{1/2}C}{R^{1/2}T^{1/2}} \tag{4}$$

D = diffusion coefficient (1×10^{-5} cm²/s assumed), v = sweep rate (0.5 V/s), C = concentration (mol/mL), R = 8.314, and T = temperature (K). [b] mA. [c] mol/mL × 10⁵.

Figure 6. Peak currents of single-sweep scans measured in sodium carbonate (900 °C) sparged with nitrogen followed by air and exhaust-gas CO_2 and O_2 concentrations plotted as functions of reaction time.

Air and Then Nitrogen Sparge. Sodium carbonate melt (900 °C) was sparged with air for 48 h and then sparged with nitrogen. The results of the nitrogen sparge are shown in Figure 7. The carbon dioxide concentration of the exhaust gas, which was equilibrated at approximately 0.05% during the air sparge, decreased slightly to approximately 0.03% when the nitrogen sparge was begun and remained at that level. The oxygen concentration of the exhaust gas decreased rapidly from 20.9% to ~0.10% over the first 60 min of the nitrogen sparge and then continued to decrease more slowly. After initially increasing slightly, cathodic wave 1 decreased rapidly (from 29.85 mA) when the nitrogen sparge was begun and was essentially absent after 35 min (0.44 mA). Cathodic wave 2 and anodic wave 6, after initially increasing, decreased steadily during the nitrogen sparge (from 12.50 to 3.49 mA and from −22.81 to −6.20 mA, respectively). Cathodic wave 3 decreased steadily from 26.75 to 2.00 mA. Anodic wave 7, after an initial slight decrease, increased rapidly over the first 76 min of the nitrogen sparge and (from −2.18 to −13.50 mA) then remained relatively constant for the remainder of the experiment.

The results show that removal of oxygen from the sparge gas (i.e., nitrogen sparge) resulted in the rapid decomposition of all of the observable species in the melt with the exception of the species responsible for anodic wave 7.

Air and Then Carbon Dioxide (1.8%) and Nitrogen (Balance) Sparge. Sodium carbonate melt (900 °C) was sparged with air for 48 h, followed by a mixture of carbon dioxide (1.8%) and nitrogen (balance). The results of the CO_2-enriched nitrogen sparge are shown in Figure 8.

The integral of the exhaust-gas carbon dioxide concentration vs. time curve indicated that 2.2 mmol of carbon dioxide was consumed over the first 100 min. This represents the maximum quantity of ionic species in the melt under the conditions capable of reacting with carbon dioxide (2.44 × 10^{-5} mol/mL). The oxygen concentration of the exhaust gas decreased from 20.9% to 0 after ~40 min. Cathodic wave 1 decreased from

Figure 7. Peak currents of single-sweep scans measured in sodium carbonate (900 °C) sparged with air followed by nitrogen and exhaust-gas O_2 concentration plotted as functions of reaction time.

Figure 8. Peak currents of single-sweep scans measured in sodium carbonate (900 °C) sparged with a mixture of carbon dioxide (1.8%) and nitrogen after air and exhaust-gas CO_2 and O_2 concentrations plotted as functions of reaction time.

27.06 to 3.37 mA in the first 10 min and then continued to decrease slowly to a final peak current of 3.10 mA after 178 min. Cathodic wave 2 and anodic wave 6 decreased from 10.16 mA and −19.27 mA to 0 over the course of the experiment. Anodic wave 7 initially increased during the first 10

Figure 9. Peak currents of single-sweep scans measured in sodium carbonate (900 °C) sparged with a mixture of carbon dioxide (1.11%), oxygen (20.9%), and nitrogen (balance) after air and exhaust-gas O_2 (−20.8%) and CO_2 concentrations plotted as functions of reaction time.

Figure 10. Peak currents of single-sweep scans measured in sodium carbonate (900 °C) sparged initially with dry air and then moist air for 68 min followed by dry air again and exhaust-gas CO_2 concentration plotted as functions of reaction time.

min from −0.35 to −7.03 mA and then slowly decreased over the remainder of the experiment to −3.64 mA. Cathodic wave 3 decreased steadily from 22.62 to 3.70 mA during the carbon dioxide/nitrogen sparge.

Air Sparge with Added Carbon Dioxide. Sodium carbonate melt (900 °C) was sparged with air for 48 h and then sparged with a mixture of carbon dioxide (1.11%), oxygen (20.9%), and nitrogen (balance). The results show the effect of increased carbon dioxide concentration (from 0.03% in air to 1.11%) with the oxygen concentration remaining constant. The results of the CO_2-enriched air sparge are shown in Figure 9.

Oxygen was evolved immediately when the CO_2-rich air sparge was started. The integral of the exhaust-gas oxygen concentration vs. time curve indicated that 0.091 mmol was evolved over the first 60 min of the experiment. The carbon dioxide concentration of the exhaust gas increased from the initial level (~0.05%) to approximately 1.0% over the first 60 min and then slowly increased to 1.11% after 400 min. The integral of the exhaust-gas carbon dioxide concentration vs. time curve corresponded to 0.133 mmol. Thus, the ratio of carbon dioxide consumed to oxygen evolved was 1.46. These results clearly indicate that the melt contained species such as peroxide ion (eq 5) and/or superoxide ion (eq 6) that react

$$O_2^{2-} + CO_2 \rightleftarrows {}^1/_2 O_2 + CO_3^{2-} \qquad (5)$$

$$2O_2^- + CO_2 \rightleftarrows {}^3/_2 O_2 + CO_3^{2-} \qquad (6)$$

with carbon dioxide to produce oxygen in addition to oxide ion, which consumes carbon dioxide without production of oxygen (eq 7).

$$O^{2-} + CO_2 \rightleftarrows CO_3^{2-} \qquad (7)$$

During the first 20 min of the CO_2-rich sparge, cathodic wave 1 decreased rapidly from 29.01 to 14.00 mA and then continued to decrease slowly to 11.14 mA over the next 350 min. Cathodic wave 2 and anodic wave 6 decreased from

22.19 and −26.28 mA to nearly 0 over the first 13 min. Anodic wave 7 initially decreased, then increased to −6.33 mA after 20 min, and decreased very slowly over the course of the experiment to −3.81 mA. Cathodic wave 3 increased from 29.70 to 31.22 mA and then decreased smoothly to 8.57 mA after 350 min.

Air Sparge with Added Moisture. Sodium carbonate melt (900 °C) was sparged with air for 18 h and then sparged with air that was passed through a water bubbler maintained at 23 °C prior to entering the melt. The results are shown in Figure 10. The moist-air sparge was allowed to continue for 68 min, and then dry air was again sparged. A gravimetric control experiment in which the water vapor from the moist-air sparge was collected by using Anhydrone showed that 9.2 mmol of water had been introduced into the melt. Cathodic wave 1 decreased from the initial value of 19.31 mA to approximately 7 mA over the first 10 min after the addition of moist air and remained relatively constant. Cathodic wave 2 and anodic wave 6 decreased rapidly from initial values of 16.94 and −17.15 mA, respectively to nearly 0 after 10 min. When the dry-air sparge was substituted for the moist air, the peak currents of cathodic waves 1 and 2 and anodic wave 6 increased. Anodic wave 7 increased slightly during the moist-air sparge and decreased during the dry-air sparge. Cathodic wave 3 decreased from 29.40 to 19.10 mA during the moist-air sparge and then increased during the dry-air sparge. The remaining waves were relatively unchanged. Approximately 1100 min of dry-air sparge was required for the waves to return to the initial values. The integral of the carbon dioxide concentration of the exhaust gas vs. time curve during the moist-air sparge indicated that 5.7 mmol of carbon dioxide had evolved.

The reaction of water vapor with carbonate ion (eq 8)

$$CO_3^{2-} + H_2O \rightarrow CO_2 + 2OH^- \qquad (8)$$

produces one carbon dioxide molecule and two hydroxide ions

Figure 11. ESR spectrum (77 K) of cooled sodium carbonate melt after oxygen sparge, indicating the presence of superoxide ion.

for each water molecule consumed, which probably accounts for most of the carbon dioxide evolved. The difference between the carbon dioxide evolved and the water vapor introduced (3.5 mmol) represents the quantity of melt species that react with water vapor without producing carbon dioxide (eq 9–11)

$$O^{2-} + H_2O \rightarrow 2OH^- \tag{9}$$

$$O_2^{2-} + H_2O \rightarrow 2OH^- + {}^1/_2O_2 \tag{10}$$

$$2O_2^- + H_2O \rightarrow 2OH^- + {}^3/_2O_2 \tag{11}$$

and/or species that react with the carbon dioxide produced (eq 5–7) from the water vapor/carbonate ion reaction (eq 8). The present data cannot distinguish between these possibilities. No "excess" oxygen and no water vapor were observed in the exhaust gas during the moist-air sparge; however, the maximum oxygen concentration that could have appeared in the exhaust gas, based upon the "excess" water introduced into the melt, would be $\sim 0.03\%$. This value compared to the $\sim 20.9\%$ oxygen in the sparge gas is within experimental error and may not have been detected.

These results indicate that, in the presence of water vapor, all of the melt species (with the exception of that responsible for anodic wave 7) decreased. No new waves appeared, which suggests that the electrochemistry of water and hydroxide ion are outside the window observed.

ESR Spectrum of Matrix-Isolated Superoxide Ion. A sample of sodium carbonate (175 g) was heated to 900 °C in an alumina tube under 1 atm of oxygen and then sparged with oxygen for 48 h. The alumina tube and its contents were removed from the furnace and allowed to cool as rapidly as possible (frozen in <5 min) while 1 atm of oxygen was maintained over the contents. The solid was removed in one piece and transferred to a drybox, and a piece from within was ground to powder and analyzed by ESR. The ESR spectrum of the powder measured at 77 K is shown in Figure 11. The following values were calculated: $g_\parallel = 2.162$ and $g_\perp = 1.997$. The general shape of the measured ESR spectrum and the calculated g values were virtually identical with the ESR spectrum of sodium superoxide in a solid matrix of sodium peroxide.[19]

Discussion

Current–potential curves of molten sodium carbonate in the potential range +0.10 to –1.40 V consist of five cathodic waves and three anodic waves (Figure 3b).

Cathodic Wave 1. Excluding the cutoff waves, the major cathodic wave observed when the sparge gas contained oxygen

($E_{1/2} = -0.47$ V) was found to represent a reversible, 1-electron transfer. The wave exhibited a strong positive dependence on oxygen pressure, a strong negative dependence on carbon dioxide pressure, and a negative dependence on water–vapor pressure. Addition of sodium superoxide to the melt caused an immediate increase in the peak current. These results suggest that the wave is due to the reversible, 1-electron reduction of superoxide ion according to eq 12. The oxygen

$$O_2^- + e^- \rightleftharpoons O_2^{2-} \tag{12}$$

and carbon dioxide dependences of the wave suggest that superoxide ion is produced in the melt by the overall process represented by eq 6. Quantitative determination of the re-

$$CO_3^{2-} + {}^3/_2O_2 \rightleftharpoons 2O_2^- + CO_2 \tag{6}$$

action orders in oxygen pressure and carbon dioxide pressure to confirm eq 6 were not obtained because steady state was not achieved under the sparging conditions of these experiments. Analysis of the dynamic data to determine reaction orders will be reported elsewhere. The presence of superoxide ion in sodium carbonate melts was clearly shown by ESR measurements of cooled melt samples (Figure 11). An alternate assignment considered for the wave is the 1-electron reduction of molecular oxygen. Such an assignment is mitigated by the fact that, with similar oxygen concentrations present in the exhaust gas (i.e., electrochemical cell) after the addition of sodium peroxide or sodium superoxide (Table II), the peak current of wave 1 was nearly 4 times greater after the addition of superoxide ion. Moreover, studies by others have shown that the concentration of dissolved molecular oxygen in carbonate melts is significantly lower than that of superoxide ion;[20-22] thus, the major wave is not likely to be due to dissolved oxygen.

Anodic Wave 7. The anodic wave observed at $E_{1/2} \sim -0.30$ V under air sparge was found to represent a 1-electron transfer. The peak current increased steadily under nitrogen sparge, exhibited negative dependences on both oxygen and carbon dioxide pressures, and increased slightly in the presence of water vapor. The addition of sodium oxide to the melt caused an immediate increase in the peak current. After addition of sodium peroxide or sodium superoxide to the melt, slightly more than stoichiometric quantities of oxygen based upon the complete decomposition of each to oxide ion were rapidly evolved, and in each case, the peak current of the wave increased. These results are consistent with the assignment of the wave to a 1-electron oxidation of oxide ion represented by eq 13. Thermodynamic calculations using JANAF data,[23]

$$O^{2-} \rightarrow e^- + O^- \tag{13}$$

however, show that the $E°$ for such an oxidation (1200 K) is +0.51 V and that the $E°$ for the oxidation of the product (eq 14) is more negative. Thus it would be expected that the

$$O^- \rightarrow e^- + {}^1/_2O_2 \tag{14}$$

oxidation of oxide ion would appear as an overall 2-electron wave (eq 15) at a potential more positive than that of the

$$O^{2-} \rightarrow 2e^- + {}^1/_2O_2 \tag{15}$$

observed wave. The anodic branch of the cyclic voltammogram of air-sparged sodium carbonate melt (Figure 3a) ex-

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hibited a $E_{1/2}$ at approximately −0.42 V. The average $E_{1/2}$ potential of the 1-electron anodic wave described above in all of the curves measured in this study was −0.40 V. On the basis of these latter peak parameter results, a more reasonable assignment of the wave is to the 1-electron oxidation of peroxide ion (reverse of eq 12). To do that, with respect to the chemical behavior of the species, it is necessary to propose that, under nitrogen-sparged conditions or under other conditions in which the melt should contain relatively large concentrations of oxide ion, significant concentrations of peroxide ion also exist.

The thermal decomposition of sodium carbonate proceeds in two steps, forming first sodium oxide and carbon dioxide (eq 16). In a second step, sodium oxide decomposes largely

$$Na_2CO_3 \rightleftharpoons Na_2O + CO_2 \qquad (16)$$

to sodium and oxygen (eq 17).[24,25] The present results suggest

$$Na_2O \rightleftharpoons 2Na + {}^1/_2O_2 \qquad (17)$$

that, under the sparged conditions of the experiments (i.e., continuous removal of sodium vapor, oxygen, and carbon dioxide), the decomposition of sodium oxide is fast enough to produce sufficient oxygen to react with the melt to form peroxide ion. The overall process of sodium carbonate decomposition under sparged conditions may then be represented by eq 18. With sparge gas containing oxygen, the equilibrium

$$2Na_2CO_3 \rightleftharpoons 2Na + Na_2O_2 + 2CO_2 \qquad (18)$$

represented by eq 17 is suppressed, and oxygen reacts with the oxide ion (eq 2) produced by the initial step of carbonate ion decomposition or with carbonate ion directly (eq 19) to

$$CO_3^{2-} + {}^1/_2O_2 \rightleftharpoons O_2^{2-} + CO_2 \qquad (19)$$

form peroxide ion and subsequently superoxide ion (eq 20).

$$O_2^{2-} + O_2 \rightleftharpoons 2O_2^- \qquad (20)$$

In single-sweep scans from the rest potential with oxygen-containing sparge gas, the anodic branch (i.e., peroxide ion oxidation) is very small compared to the cathodic branch (superoxide ion reduction) (Figure 3b). This suggests that superoxide ion is favored under such conditions.

Cathodic Wave 2 and Anodic Wave 6. The 1-electron reversible wave described above, which is assigned to the superoxide ion/peroxide ion couple, is superimposed upon a 2-electron reversible wave composed of cathodic wave 2 and anodic wave 6. This is evidenced by the cathodic and anodic peak separation of the observed reversible wave (under air sparge) that corresponded to $n = 1.17$ (Figure 3). Moreover, after the addition of oxide ion to the melt under argon sparge, a reversible wave became dominant with the cathodic and anodic peak separation corresponding to $n = 2.47$ (Figure 5). In the computer-derived waves, both the cathodic (wave 2) and anodic (wave 6) branches exhibited positive dependences on oxygen and negative dependences on carbon dioxide and water vapor. The addition of sodium oxide to the melt resulted in a peak current increase of only the anodic branch, while addition of sodium peroxide or sodium superoxide caused an increase of both the cathodic and anodic branches of the wave. The cathodic branch cannot be due to a 2-electron reduction of peroxide ion, which would preclude the observed reversibility of the 1-electron reduction of superoxide ion (eq 12). That is, if the 1-electron reduction of superoxide ion to peroxide ion were followed immediately by reduction of peroxide ion, the concentration of peroxide ion at the electrode surface would be depleted and its oxidation on the reverse scan would not

be observed. However, the results above suggest that cathodic wave 2 behaves like peroxide ion. A likely possibility is that the species responsible for cathodic wave 2 is the carbon dioxide adduct of peroxide ion, peroxycarbonate ion (eq 21)

$$O_2^{2-} + CO_2 \rightleftharpoons CO_4^{2-} \qquad (21)$$

(analogous to carbonate ion, the oxide ion adduct of carbon dioxide). The 2-electron reversible wave may then be represented by eq 22. It follows that the anodic branch of the

$$CO_4^{2-} + 2e^- \rightleftharpoons CO_3^{2-} + O^{2-} \qquad (22)$$

reversible wave is the oxidation of oxide ion in the presence of carbonate ion. This is consistent with the observed peak current increase of the anodic branch during nitrogen sparge (i.e., increase in oxide ion concentration) and after addition of oxide ion. Peroxycarbonate ion may be produced in the melt by the reaction of peroxide ion with carbon dioxide (eq 21) and/or by reaction of oxygen with carbonate ion (eq 23).

$$CO_3^{2-} + {}^1/_2O_2 \rightleftharpoons CO_4^{2-} \qquad (23)$$

Adducts of peroxide ion and superoxide ion with carbon dioxide including peroxycarbonate and peroxydicarbonate $(C_2O_6^{2-})$ have been reported,[26,27] the possible existence of peroxycarbonate in molten carbonates has been suggested,[28] and organic derivatives of peroxycarbonate are known.[29]

Cathodic Wave 3. The 2-electron irreversible cathodic wave observed at approximately −1.06 V (Figure 3b) exhibited a positive dependence on oxygen and negative dependences on carbon dioxide and water vapor. The addition of sodium oxide, sodium peroxide, or sodium superoxide to the melt under nitrogen sparge had little effect on the wave. After the melt was sparged with air to build up the wave, it was found that the peak current decreased under subsequent sparges with nitrogen (Figure 7), with nitrogen that contained carbon dioxide (1.8%) (Figure 8), with nitrogen that contained carbon dioxide (1.11%) and oxygen (20.9%) in which the oxygen concentration was held constant (Figure 9), and with moist air (Figure 10). The wave is not related to the product of wave 1 (i.e., peroxide ion) since the peak currents of the two waves vary independently. These results appear to preclude carbon dioxide, oxygen, peroxide ion, and water vapor (and related species, e.g., hydroxide ion) from being responsible for wave 3. With those species eliminated and superoxide ion and peroxycarbonate ion already assigned, the most reasonable possibility remaining is that wave 3 is due to the 2-electron reduction of peroxydicarbonate ion (eq 24). Such a species

$$C_2O_6^{2-} + 2e^- \rightarrow 2CO_3^{2-} \qquad (24)$$

may be produced in the melt by successive addition of carbon dioxide to peroxide ion (eq 21 and 25) and/or by reaction of oxygen with carbonate ion (eq 23) to form peroxycarbonate ion followed by reaction with carbon dioxide (eq 25).

$$CO_4^{2-} + CO_2 \rightleftharpoons C_2O_6^{2-} \qquad (25)$$

Cathodic Wave 4. The cathodic wave at ∼−1.24 V (Figure 3b) was observed directly in only a few of the single-sweep scans. It was found, however, that such a wave was necessary to obtain good computer fits of the experimental curves in the −1.0 to −1.4 V region and that the best fits were obtained with the wave representing a 2-electron transfer. The wave changed

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Table III. Assignments of Waves Observed in Molten Sodium Carbonate

wave	E_p, V^a	eq
1	-0.50	$O_2^- + e^- \rightarrow O_2^{2-}$
2	-0.49	$CO_4^{2-} + 2e^- \rightarrow CO_3^{2-} + O^{2-}$
3	-1.00	$C_2O_6^{2-} + 2e^- \rightarrow 2CO_3^{2-}$
4	-1.20	?
5	<-1.40	$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-}$ [b]
6	-0.40	$CO_3^{2-} + O^{2-} \rightarrow 2e^- + CO_4^{2-}$
7	-0.31	$O_2^{2-} \rightarrow e^- + O_2^-$
8	>0.10	$CO_3^{2-} \rightarrow 2e^- + {}^1/_2O_2 + CO_2$ [c]

[a] Reference, 33% O_2, 67% CO_2, Au.　[b] Reference 7.
[c] Reference 6.

Table IV. Proposed Sequence of Reactions

eq	K_e
$Na_2CO_3 \underset{12}{\overset{9^a}{\rightleftharpoons}} Na_2O + CO_2$　(16)	9.7×10^{-8} [b]
$Na_2O \underset{14}{\overset{11}{\rightleftharpoons}} 2Na + {}^1/_2O_2$　(17)	2.6×10^{-11} [b]
$Na_2CO_3 + {}^1/_2O_2 \underset{2}{\overset{1}{\rightleftharpoons}} Na_2CO_4$　(23)	1.6×10^{-11} [c]
$Na_2CO_4 \underset{3}{\overset{4}{\rightleftharpoons}} Na_2O_2 + CO_2$　(21)	1.8×10^4 [c]
$Na_2CO_4 + CO_2 \underset{5}{\overset{6}{\rightleftharpoons}} Na_2C_2O_6$　(25)	7.8×10^1 [c]
$Na_2O_2 + O_2 \underset{13}{\overset{10}{\rightleftharpoons}} 2NaO_2$　(20)	4.4×10^{-3} [b]
$Na_2O_2 \underset{8}{\overset{7}{\rightleftharpoons}} Na_2O + {}^1/_2O_2$　(2)	3.4×10^{-1} [b]

[a] Estimated relative rate constant (1 smallest). [b] Equilibrium constants calculated from JANAF data[23] (1200 K). [c] Estimated.

very little under the various experimental conditions employed in this work (Figures 5–10), and therefore no assignment can be made at this time.

Cathodic and Anodic Cutoff Waves (Waves 5 and 8). Because of the high peak currents of the cutoff waves, no attempt was made to obtain good computer fits. The cathodic cutoff wave has been assigned previously to the 2-electron reduction of carbon dioxide (>700 °C) according to eq 26.[7] The anodic

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-} \qquad (26)$$

cutoff wave is probably due to the oxidation of carbonate ion according to eq 27.[6]

$$CO_3^{2-} \rightarrow 2e^- + {}^1/_2O_2 + CO_2 \qquad (27)$$

Proposed Sequence of Reactions. Assignments consistent with the data are listed in Table III, and a proposed sequence of reactions is shown in Table IV that accounts for the interconversion of melt species. The data provide the basis for estimating the relative rates of the reactions. Calculated equilibrium constants for eq 2, 16, 17, and 20 show that the rates of the forward reactions (k_f) are less than the corresponding reverse reactions (k_r) (unit activity assumed, eq 28).

$$K_e = k_f/k_r \qquad (28)$$

A crude estimate of the free energy of formation of sodium peroxycarbonate and sodium peroxydicarbonate (for which no thermodynamic data are available) was made by assuming that $E°$ values for the reduction reactions are approximately equal to the measured $E_{1/2}$ (eq 29). The estimated free

$$\Delta G = -nFE \qquad (29)$$

energies ($\Delta G \approx -132$ kcal/mol for sodium peroxycarbonate and -237 kcal/mol for sodium peroxydicarbonate) were then used to calculate approximate equilibrium constants of the reactions involving sodium peroxycarbonate (eq 21, 23, and 25) and sodium peroxydicarbonate (eq 25). The estimated equilibrium constants suggest that for eq 21 and 25 $k_f > k_r$ and the opposite is true for eq 23.

Under nitrogen sparge, the decomposition reactions of carbonate ion (eq 16) and oxide ion (eq 17) proceed to the right, the driving force being the continuous removal of the volatile products (carbon dioxide, sodium vapor, and oxygen). The oxygen produced by oxide ion decomposition (eq 17) reacts with carbonate ion, forming peroxycarbonate ion (eq 23) in a relatively slow step. In a subsequent fast reaction, peroxycarbonate ion decomposes to peroxide ion and carbon dioxide (eq 21). Very little peroxycarbonate ion was observed during nitrogen sparge (Figure 4), which suggests that k_f of peroxycarbonate formation (eq 23) is less than k_f of its decomposition (eq 21). Furthermore, the rapid increase in peroxide ion concentration suggests that k_f of peroxycarbonate ion decomposition to peroxide ion (eq 21) is greater than its rate of decomposition to carbonate ion and oxygen (k_r, eq 23). The concentration of peroxide ion was greater than that of oxide ion, which requires k_f of oxide ion decomposition (eq 17) to be greater than k_f of carbonate ion decomposition (eq 16) such that the initial products of carbonate ion decomposition are peroxide ion and carbon dioxide (eq 18). The subsequent increase in oxide ion concentration is probably due to the peroxide ion/oxide ion equilibrium represented by eq 2. The concentration of peroxide ion was sufficiently low that apparently it could not compete successfully with carbonate ion for the available oxygen, and therefore no superoxide ion was observed (eq 20). The concentrations of carbon dioxide and peroxycarbonate ion were low during nitrogen sparge, which minimized the forward reaction of eq 25, and thus, no significant concentration of peroxydicarbonate ion was observed.

The addition of oxygen to the sparge gas (air sparge) caused an immediate increase in the superoxide ion and oxide ion concentrations, a slow increase in the peroxycarbonate and peroxydicarbonate ion concentrations, and a decrease in the peroxide ion concentration (Figure 6). These results indicate that the reaction of oxygen with peroxide ion is rapid (k_f, eq 20). The increased oxygen concentration apparently suppressed the decomposition of oxide ion (k_f, eq 17), which allowed the buildup of oxide ion in the melt. Such a buildup of oxide ion requires that its reaction with oxygen (k_r, eq 2) be slower than its production by carbonate ion decomposition (k_f, eq 16). The initial decrease in peroxide ion concentration is probably due to its rapid reaction with oxygen, producing superoxide ion (k_f, eq 20); however, the fact that it failed to increase later in the experiment when superoxide ion and oxide ion approached steady state is not clear. A possible explanation is that the melt became saturated with oxide ion (oxide precipitation?) at a concentration sufficiently low that the equilibrium represented by eq 2 lies to the right.

The removal of oxygen from the sparge gas (nitrogen sparge after air sparge) caused an immediate decrease in the superoxide ion concentration, an initial decrease in the peroxide ion concentration, and an initial increase in the oxide ion concentration (Figure 7). This reflects the large k_r of reaction 20 and k_f of reaction 2, the decompositions of superoxide and peroxide ions that ultimately produce oxide ion. The removal of oxygen allowed the decomposition of oxide ion to proceed (k_f, eq 17), which accounts for the subsequent decrease in oxide ion concentration and the buildup of peroxide ion. Similarly, the peroxycarbonate ion (after a slight increase) and the peroxydicarbonate ion concentrations both decreased during the experiment, consistent with the proposed mechanism suggested above for the nitrogen-sparged experiment.

The removal of oxygen from the sparge gas with a simultaneous increase in carbon dioxide concentration (Figure 8) caused immediate decreases in the concentrations of superoxide ion and oxide ion. The rate of superoxide ion decomposition was nearly the same with pure nitrogen sparge (Figure 7) as with nitrogen that contained carbon dioxide (Figure 8), which suggests that the rate is independent of carbon dioxide. The rate of oxide ion consumption, on the other hand, is clearly dependent on carbon dioxide, as shown by the increased rate of consumption in the presence of carbon dioxide. These results are consistent with the rate of oxide ion reaction with carbon dioxide (k_r, eq 16) being greater than the rate of decomposition (k_f, eq 17). The decrease in peroxycarbonate ion concentration was faster when the nitrogen sparge gas contained carbon dioxide rather than being pure nitrogen. This supports the proposed reaction of peroxycarbonate ion with carbon dioxide to produce peroxydicarbonate ion (eq 25). Indeed, the decrease in the concentration of peroxydicarbonate ion was slightly slower with CO_2-containing sparge gas. The peroxide ion concentration initially increased due to the decomposition of superoxide ion and then slowly decreased throughout the experiment. Thus, with carbon dioxide in the sparge gas, the concentration of oxide ion was low (k_r, eq 16), which, in turn, suppressed the reactions discussed above that produced peroxide ion during pure nitrogen sparge.

Enrichment of carbon dioxide in the sparge gas while the oxygen concentration was maintained constant caused a rapid decrease in the concentrations of oxide ion and peroxycarbonate ion (Figure 9). Superoxide ion and peroxydicarbonate ion decreased more slowly. This suggests that oxide and peroxycarbonate ions react directly with carbon dioxide while superoxide and peroxydicarbonate ions may not. The decrease in oxide ion concentration allowed the decomposition of peroxide ion (k_f, eq 2) and thence the decomposition of superoxide ion (k_r, eq 20), which accounts for the evolution of oxygen. The fact that the peroxide ion concentration remained relatively constant initially and then increased suggests that the rate of superoxide ion decomposition to oxygen and peroxide ion is faster than that of peroxide ion decomposition.

The addition of water vapor to air sparge gas had approximately the same effect on the concentrations of the melt species as did the addition of carbon dioxide (Figures 9 and 10). This suggests that most of the water vapor reacted with carbonate ion to produce carbon dioxide and hydroxide ion (eq 8). The changes observed in the other melt species are consistent with the resultant increased carbon dioxide concentration.

Proposed Reference-Electrode Mechanism. It is generally accepted that the overall reaction of the oxygen/carbon dioxide reference electrode in carbonate melts is represented by eq 27.

$$^1/_2O_2 + CO_2 + 2e^- \rightleftharpoons CO_3^{2-} \qquad (27)$$

Borucka has shown that the reaction is reversible and follows the corresponding Nernst equation (eq 30).[17] It was confirmed in this work that rest potentials of sodium carbonate melts under a 28-element matrix of sparge-gas mixtures ranging from 2 to 90% oxygen and 0.07 to 5% carbon dioxide

$$E = E^\circ + \frac{RT}{2F} \ln (P_{O_2}^{1/2} P_{CO_2}) \qquad (30)$$

(balance nitrogen) could be predicted to within ± 10 mV by employing eq 30. Although the characteristics of the oxygen/carbon dioxide reference electrode are understood and the electrode is widely used, the mechanism of the overall reaction is apparently unknown.

On the basis of the results of this work, a likely possibility involves the reversible reduction of peroxycarbonate ion, which produces oxide and carbonate ions (eq 22). The production of peroxycarbonate ion arises from the reaction of oxygen with carbonate ion (eq 23). The oxide ion produced by reduction

$$CO_3^{2-} + {}^1/_2O_2 \rightleftharpoons CO_4^{2-} \qquad (23)$$

$$CO_4^{2-} + 2e^- \rightleftharpoons O^{2-} + CO_3^{2-} \qquad (22)$$

$$O^{2-} + CO_2 \rightleftharpoons CO_3^{2-} \qquad (16)$$

of peroxycarbonate ion reacts with carbon dioxide, forming carbonate ion (eq 16). The rest potentials measured in this work were invariably within the cathodic and anodic branches of the reversible 2-electron couple CO_4^{2-}/O^{2-}, CO_3^{2-} (eq 22). In recent studies using nickel oxide electrodes, current–density measurements near the rest potential exhibited oxygen and carbon dioxide dependences of 0.625 and 0.250, respectively, for cathodic currents and 0.125 and -0.750, respectively, for anodic currents.[12] These values are reasonably close to the theoretical values expected of the proposed mechanism (i.e., 0.5 and 0 for cathodic currents and 0 and -1 for anodic currents, respectively, for oxygen and carbon dioxide dependences). Inspection of Table IV shows that the concentrations of peroxycarbonate and oxide ions, the primary electroactive species in this mechanism, are both dependent on oxygen and carbon dioxide pressure. Although the reactions represented by eq 16 and 23 are probably the dominant steps in the formation of peroxycarbonate and oxide ions, the other reactions listed in Table IV may also participate. The apparent reaction orders with respect to oxygen and carbon dioxide depend on all of the reactions involved in the formation and decomposition of peroxycarbonate and oxide ions. The deviations between the measured dependences[12] and the theoretical dependences that are based only on eq 16 and 23 suggest the extent of the participation of the other reactions shown in Table IV.

Time-dependent studies, in addition to those presented here and a rigorous analysis of the data, are in progress. The work is directed toward determining kinetic parameters associated with the formation and decomposition of the melt species described here and how these parameters are related to the oxidation of graphite in sodium carbonate melt. The results will be reported elsewhere.

Registry No. Sodium carbonate, 497-19-8; oxygen, 7782-44-7; carbon dioxide, 124-38-9; water, 7732-18-5; oxide, 16833-27-5; superoxide, 11062-77-4; peroxide, 14915-07-2; carbon, 7440-44-0; nitrogen, 7727-37-9; sodium oxide, 1313-59-3; sodium peroxide, 1313-60-6; sodium superoxide, 12034-12-7; gold, 7440-57-5; alumina, 1344-28-1.