Production of Carbon Monoxide by Means of Molten Salt Electrolysis

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1 Introduction

The accumulation of carbon dioxide in the world environment is cautioned to cause various kind of undesirable effects to meteorology as well as ecology. In addition, the shortage in both energy and natural resources is now a big problem in many countries. Because of these backgrounds, studies on the utilization of carbon dioxide have been in progress at many places from various view points.

In this report, we should like to propose a new technique for producing carbon monoxide at moderate temperatures. The process is simply composed of electrolysis of molten carbonate salt with a carbon anode. It can be said that the process is, in some sense, a variation of Boudouard reaction, which is expressed by the equation,

Under the atmospheric pressure, the equilibrium of eq. (1) lies about 700°C, above which the equilibrium inclines towards right hand side and carbon monoxide predominates. Kinetic natures of the reaction have been thoroughly studied by many authors¹⁻⁵⁾. The rate of conversion (equilibration) is, however, not sufficiently rapid and a temperature exceeding 1000°C is necessary for industrial purposes. The slowness of the reaction rate may be attributed to that the reaction takes place at a heterogeneous gas solid interface. Accordingly, if it is possible to carry out the reaction in some condensed phase, a marked acceleration of reaction velocity will be expected.

We attempted to realize the idea in the following way.

Thermochemistry of some carbonates

Prior making experimental study, we surveyed

thermochemical character of carbonate salts of various metal cations in the literature⁶⁾ to obtain the free energy data for the following reactions.

where M stands for metal elements. ΔG values for several metal carbonates were calculated. As regard to all alkali metal salts used, all the reactions have positive ΔG values at temperatures less than 1000°C indicating that no spontaneous production of carbon monoxide is expectable. This, in turn, indicates that external supply of some energy is necessary^{*1}. The employment of electrolysis was thus attempted.

2 Experiments

In order to get a low temperature melt, a ternary equimolar mixture of lithium, sodium and potassium carbonates was used as the molten electrolyte. The phase diagram of this system is available⁷⁾. Electrode materials used were a nickel plate for the cathode electrode and graphite or amorphous carbon rod for the anode electrode, respectively.

Several types of container (reaction vessel) have been examined trially but fixed finally to the apparatus shown in Fig. 1. Outer jacket (1) is of 99% alumina tube having dimensions of 30 mm *i.d.* and 350 mm in height. The gas space over the melt was separated by means of a porcelain tube (2) for cathode and anode compartments. The whole apparatus was immersed in an electric furnace and the temperature of which was controlled within $\pm 10^\circ\text{C}$ at every temperatures of interest. Electrolysis was done under the constant current condition (total cell current 100 mA).

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*1 This statement needs some correction. Further details will be given in the succeeding paper⁹⁾.

Fig. 1 Reaction Vessel

- (1): Outer jacket of 99% Al_2O_3 tube.
- (2): Porcelain separator
- (3): Nickel cathode
- (4): Carbon anode
- (5): Silicone rubber stopper

To each compartment, pyrex tubings were attached for both gas inlet and outlet. The outlet tubing was connected to a 500 cm^3 gas buret which stored all the gas evolved. The composition of gas evolved was analysed periodically with a gas chromatograph. Before each experiment, gases over the melt were completely substituted by helium. The melt was, however, unchanged throughout the whole experiment. Reproducibility was sufficient for repeated runs.

3 Results

Anode reaction

Measurements were made at every 100°C in the range from 550 to 850°C. When graphite electrode was used, the gas produced was exclusively carbon dioxide and no monoxide was observed at 550°C. At 650 and 750°C, carbon monoxide appeared in the gas but the percentage was still low (1% and 20%, respectively). At 850°C, however, the production of carbon monoxide predominated (70%). The

Fig. 2 Gas evolution at 750°C (a) and 850°C (b)

Δ : Rate of gas evolution (right hand scale)
 ---: Calculated line for the rate of 0.75 mol/F
 Anode material: Graphite, Current: 100 mA
 Partial pressure is that in the presence of He

rate of gas evolution was roughly in agreement with 0.75 mol/Faraday in all experiments. The results at 750 and 850°C are shown in Fig. 2, where dotted line indicates the rate of gas evolution at 0.75 mol/F.

When graphite was substituted by amorphous

Fig. 3 Gas evolution at 750°C with use of amorphous carbon anode

(a): Partial pressure, (b) Rate of gas evolution
 Broken line indicates calculated rate after correction for thermal decomposition. T.D. stands for spontaneous thermal decomposition. Electrolysis has been started after purging the gas evolved by spontaneous decomposition. Thermal decomposition was measured for one hour before applying electrolysis. After that all the gas evolved was purged with flowing He and electrolysis started

Fig. 4 Composition of gas evolved from amorphous carbon anode

carbon (supplied by Nippon Carbon Co. Ltd.), a marked change was observed. A part of results observed are shown in Figs. 3 and 4. Noticeable points are as follows.

1) Even at 650°C, an appreciable amount of CO is evolved upon electrolysis.

2) At 750°C, evolution of CO predominates over CO₂ and 80% of the gas evolved is carbon monoxide.

3) Spontaneous thermal decomposition of carbonate melt occurs appreciably at 750°C, which was overlooked in the case of graphite.

Roughly speaking, amorphous carbon gives results equivalent to those of graphite working at a higher temperature by an amount of 100°C.

Cathode reaction

At lower temperatures, 550 to 650°C, no gas evolution was observed from the cathode reaction. At 850°C, however, a minor amount of gas evolution was observed regardless of anode materials. Major component was carbon monoxide in this case.

4 Discussion

Detailed nature of the reaction mechanism is, of course, not discernible from the above observations. Only things we can talk about is the overall reaction sequence. The reactions occurring at the anode electrode may be expressed as follows.

$\text{CO}_3^{2-} = \text{CO}_2 + 1/2 \text{O}_2 + 2e$ (6)
and, if electrode carbon is incorporated in the

reaction

When reaction proceeds via either eq. (6) or (9), then the gas evolution rate should be 0.75 mol/Faraday. The figure should be 1.5 and 1.0 for the reactions (7) and (8), respectively.

In almost all cases studied, the evolution rates were near to 0.75 mol/F. No appreciable oxygen was detected in the gas indicating that the reaction (9) is occurring at lower temperatures. From the mechanistic view point, however, we rather prefer to express the reaction by eq. (6). Oxygen appearing in the right hand side is thought to be chemisorbed on the electrode. In Boudouard reaction, many workers¹⁻⁴⁾ showed that oxygen liberated from carbon dioxide is trapped on the carbon surface at least at temperatures less than 900°C. Gasification of the oxygenated carbon complex thus produced occurs only slowly. Janz⁸⁾ reported that anodic oxidation of molten carbonate at platinum anodes is also expressed by (6). The oxygen adsorbed will detach from the surface in dual ways according to the temperature employed.

At lower temperatures, the reaction (10L) will occur mainly but will be replaced by (10H) with increasing temperature. This is consistent to the results observed. If, however, the reaction is composed of merely (6) and (10H), the CO content should not exceed 50% in the gas evolved. This was not the case at higher temperatures where the CO content was 80 percent and the rate of gas evolution exceeded 0.75 mol/F even after correcting for the spontaneous decomposition (see Fig. 4). Undoubtedly, CO₂ produced electrolytically by eq. (6) undergoes ordinary Boudouard reaction with electrode carbon. In such a situation, the overall reaction becomes to eq. (7).

In the cathode reaction with use of a nickel electrode, an accumulation of carbon black was always observed on the nickel surface even when no gas evolution was observed. This may be a result of the thermal decomposition (eq. (5)). It is plausible, that minor amount of alkali carbonate decomposes to carbon dioxide

even at temperatures around 550°C. Since the primary cathodic product is no doubt metallic sodium, carbon dioxide decomposed will react with it.

The predominant evolution of carbon monoxide found in the 750°C experiment can be explained by assuming the disproportionation between CO₂ formed by thermal decomposition and carbon accumulated by the manner of eq. (11). At higher temperatures (>750°C), it is more likely that the following direct decomposition predominates.

Under the condition of the present study, the cell voltage applied were 2.6, 2.0, 1.5 and 0.9 volts depending on the temperature 550, 650, 750 and 850°C, respectively. The data at 850°C indicates that approximately 41 moles of carbon monoxide are produced for the energy consumption of 1 kWh. The possibility of improving

this product to energy ratio still remains since no attention has been given in the cell design.

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講演内容はすでに会告にテーマが載っていたので重複しないように簡単に紹介する。機能化薄膜の第一として、アルミニウムの陽極酸化皮膜につき、小岩五中の水木氏がいろいろな用途(誘電体、光物性、電子物性、磁性、吸湿性、感光材、透過膜など)の実例を紹介した。特に最後に行なったエレクトロルミネッセンスの実験はその幻想的な光に認識を新たにしたいようだ。

次に帝人の岡庭氏が SnO₂ と In₂O₃ を蒸着した PET フィルムの特性と用途、問題点などを豊富な資料を紹介しながら解説した。今後太陽熱利用暖房の窓ガラス、吸収板などとして、省エネルギー時代にふさわしい有望な材料となるだろうとの感じを受けた。

次のテーマは表面の測定法に関することであり、東北大学工学部の末高氏が赤外、特に偏光赤外線を用いる薄膜ないし吸着層の化学種の同定法について分子レベルのオーダーでの話しをされた。赤外分析と相補的な役割を示すレーザーラマン分光についても新しくふうされた装置を示しながら解説された。最後の講演は日立製作所の森下氏により、光導電性有機皮膜の製法と電子写真への応用であった。有機皮膜の物性を目的に合うようにす

るために二重構造とし、チャージキャリアを発生させる層とチャージを保持する層とに分けて目的とする性能をもたせると言うものである。

以上のように薄膜の利用についての学術的および技術的な最高レベルの話しをきくことができ、参加者は皆大変有意義だったと感想をもらしていた。

最後に本協会としては少々残念なことではあるが次のような意見があった。今回の話題に関する文献の引用がほとんど電化誌ではなく、応用であるとか、アメリカの電化誌など他誌が圧倒的に多かったと言うことである。毎年の講演大会ではこのような内容の発表もかなりあるのに、報文として出てこないのはなぜだろうかと言う疑問である。この辺について協会、特に編集委員会として少し考えてもらいたいとの声があった。

参加者層は関東から東北にかけての会社、研究機関、大学などから若年層が多く、一度出席するとこの会のふんい気が良いのか何度も出席する方が多い。来年もおそらく同じ頃開催されることと思うが、今まで会告を見落していた方はぜひお見逃さないよう、9月号か10月号に載っています。

(N. B. 記)