

An Investigation of the Catalytic Effect with $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ Perovskite in a Sealed-off CO_2 Laser

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To improve the lifetime and output power in a sealed-off CO_2 laser, a series of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.40, 0.50, 0.60, 0.75$) perovskite-type compounds has been synthesized and used for a cathode material. Using a typical method samples were sintered at 1150°C and their structures were determined as a cubic form by means of XRD analysis. The degrees of CO_2 dissociation were measured by PAS (photoacoustic spectroscopy) with the lapse of time. In the case of $\text{Nd}_{0.4}\text{Sr}_{0.6}\text{CoO}_3$, which showed the highest catalytic cathode effect, only 7% of the initial CO_2 concentration were dissociated at 30 torr of gas mixture and 5 mA of discharge current. The more the gas pressure decreased and the discharge current increased, the more the degree of dissociation occurred. The ability of catalytic cathode to regenerate CO_2 in the laser cavity lies in order for x , $0.60 > 0.50 > 0.40 > 0.75 > 0.25 > 0.0$. Except for the case of $x=0.0$ the amounts of CO_2 dissociation were found to be within 7-15% of the initial CO_2 concentration.

Introduction

Sealed-off CO_2 laser has a lot of merits over others. It has, however, some problems unopened. These come mainly from relatively low ionization potential of CO_2 , i.e., 3.75 eV, which causes reduction of CO_2 concentration and decrease of output power¹. Therefore, the maintenance of output power depends on how to keep CO_2 concentration high enough; how to recombine the dissociated CO and oxygen species efficiently; and how to keep the reactants and products from adsorbing on metal surface used as electrodes². Several kinds of methods have been attempted to settle these problems. One of them is the application of catalytic electrode functioning both as electrode and catalyst at the same time³.

Such catalytic electrode should meet some requiring conditions; the enough conductivity to afford discharge between two electrodes and the capability to oxidize CO molecules resulting from dissociation reactions, etc.. In general, perovskite-type oxide, especially $\text{Ln}_{1-x}\text{M}_x\text{CoO}_3$ (La: lanthanides, M: alkaline earth metal), is known to have a metallic conductivity⁴ and a strong catalytic activity for the oxidation of CO into CO_2 at temperatures higher than 200°C within discharge free condition^{5,6}. In these compounds, effects of substitution of alkaline metal give rise to oxidize the Co^{3+} species to Co^{4+} in part and increase the conductivity^{7,8}. And catalytic power has been caused from the oxygen vacancy that exist in the lattice of solid structure. On the basis of this, Karube *et al.*⁵ has tested the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ as a catalytic cathode and succeeded in the suppression of CO_2 dissociation in the discharge tube. And $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ ($x=0.3$) was found to be the best among them.

Hikes *et al.*¹⁰ reported that the conductivity of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ series ($10^0\text{-}10^4/\Omega\cdot\text{cm}$)¹⁰ was comparable with that of $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ ($\sim 10^3/\Omega\cdot\text{cm}$) series^{9,10}. Moreover the catalytic ability of the latter to oxidize CO into CO_2 is similar to this series¹¹ in discharge free condition. Namely, $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ series could be a candidate as a catalytic cathode to replace the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ electrode. Here, we examine the performance characteristics of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ series as a catalytic cathode and determine the optimum x value at which shows the

most enhanced catalytic activity.

Experimental

Preparation of Electrode. Solid solutions of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ were synthesized by ordinary ceramic techniques. For starting materials, metal oxides of Nd_2O_3 , SrCO_3 , and Co_3O_4 were used. The appropriate amounts of the reagents were weighed stoichiometrically and then mixed homogeneously for 2 hours or more. Prefiring was performed at 900°C for 12 hours and followed by grinding again. Power was grinded finely and then pressed into a 3-4 mm thick pellet under 3.5 ton/cm^2 and sintered at 1150°C for 1 day. During the sintering, contraction of crystal took place, which enabled to fix the copper electrodes inserted in the hole made on metal oxide. Cooling was proceeded slowly in the furnace. Structures of the compounds were determined using X-ray diffractometer (Philips, 1710, $\text{CuK}\alpha$) equipped with a curved graphite monochromator in the selected beam path at room temperature. The homogeneity of electrode surface was examined by the SEM (Scanning Electron Microscope) technique.

Measurements of CO_2 Concentration. Discharge experiments were carried out with the laser tube in which each anode and cathode were made of copper, $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x=0.0, 0.25, 0.40, 0.50, 0.60, 0.75$) sintered at 1150°C , respectively. Prior to the experiment, cathode materials were pretreated in a vacuum condition to remove impurities. Mixture of gases ($\text{CO}_2 : \text{N}_2 : \text{He} = 1 : 1 : 8$) was charged to 30 torr in the laser tube and discharged with the current of 5 mA.

The CO_2 concentration change with the discharge time was measured by means of photoacoustic technique and discharge was proceeded further until there was no more change of CO_2 concentration. Experiments were repeated at various gas pressures and discharge currents.

Results and Discussion

Structure of Samples. Based on powder X-ray diffrac-

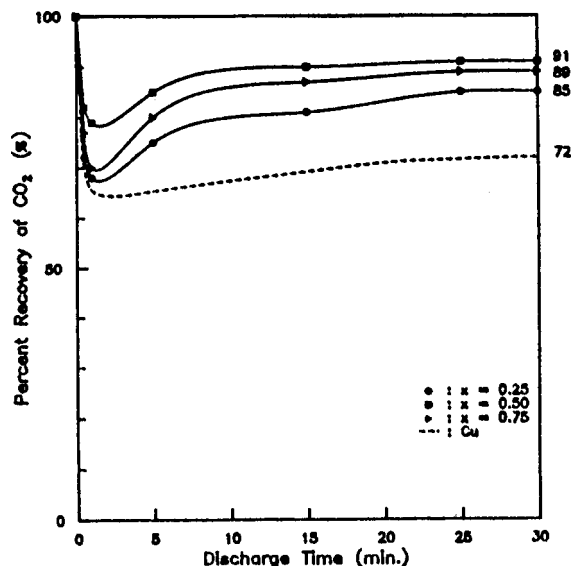


Figure 1. Change of CO_2 partial pressure on discharge time (min.) in the $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ cathode tube for three different x values and Cu. The measurements were made at the constant total pressure of 30 torr and discharge current of 5 mA.

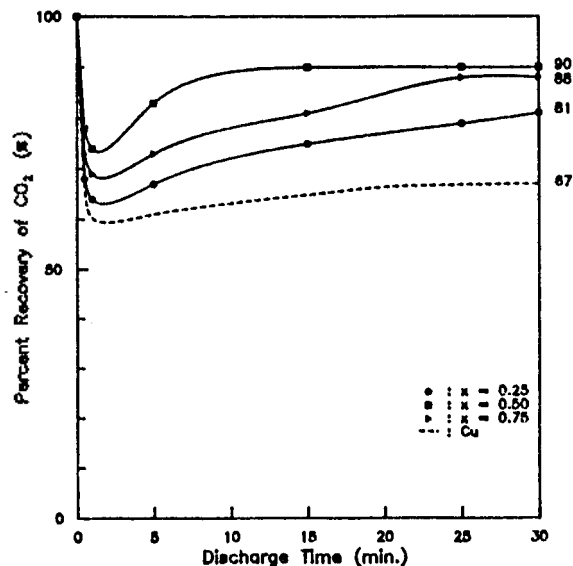


Figure 2. Change of CO_2 partial pressure on discharge time (min.) in the $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ cathode tube for three different x values and Cu. The measurements were made at the constant total pressure of 20 torr and discharge current of 5 mA.

tion data, the structures of the synthesized samples could be determined to be a cubic form. The lattice parameter constants of the compounds were increased with increasing x value such as 7.548 ($x=0.0$), 7.581 ($x=0.25$), 7.625 ($x=0.50$), and 7.679 ($x=0.75$). Note that amounts of x value means the degree of substitution of Sr^{2+} for Nd^{3+} . Considering the fact that ionic radius of Sr^{2+} (144 pm) is larger than that of Nd^{3+} (127 pm), the relationship between x and a is easily predictable. From the SEM data, we could confirm that the surface of all electrodes was homogenous.

Catalytic Effects of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$. For the pure Nd-

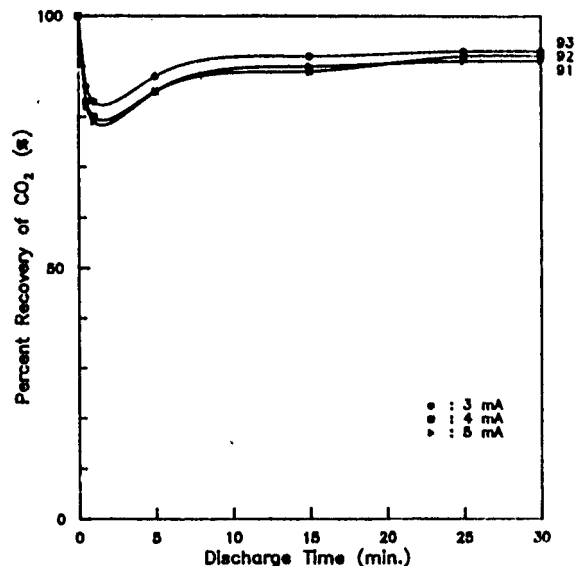


Figure 3. Change of CO_2 partial pressure on discharge time (min.) in the $\text{Nd}_{0.50}\text{Sr}_{0.50}\text{CoO}_3$ cathode tube for three different currents. The measurements were made at the constant total pressure of 30 torr.

CoO_3 ($x=0.0$) electrode it was impossible for us to investigate the catalytic effects because of the excessive heat production during the discharge caused by low conductivity.

Figure 1 shows that the temporal profile of the relative concentration of CO_2 , i.e. percent ratio of CO_2 pressure to its initial value, depends on discharge time. When 30 torr of gas mixture and 5 mA of discharge current were used, the remaining CO_2 concentration reached minimum in 1 minute for all x values of 0.25, 0.50, and 0.75 and the degrees of dissociation were 31%, 21%, and 30%, respectively. This result is not, however, satisfactory when compared with the case of Cu (copper) cathode, 36%. Meanwhile it was 15%, 9%, and 11%, respectively in 25 minute, where the catalytic effects could not be improved further. This indicates that $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$ has outstanding catalytic effects over copper's (28%) at the same condition. Fig. 2 depicts the change of CO_2 partial pressure with time. In this figure, the percent recovery of CO_2 are plotted for the perovskite and copper system at 20 torr. Comparing Figure 1 and Figure 2, more CO_2 dissociation occurred as less gas mixture filled.

Figure 3 shows the change of CO_2 concentration at three different discharge current. The degree of dissociation increased as higher discharge current was used.

As shown in Figure 4 the degrees of CO_2 dissociation vary with the x values. In the case of $\text{Nd}_{0.4}\text{Sr}_{0.6}\text{CoO}_3$ with the highest catalytic cathode effect, only 7% of the initial CO_2 concentration was consumed when 30 torr of gas mixture and 5 mA of discharge current were applied. This value is comparable with 10% for $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ within the error range.

These considerable catalytic effects can be attributed to the features of perovskite-type compounds which contain excessive O_2 supplied for the reproduction of CO_2 through the desorption-adsorption process. In the system of $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_3$, the difference of catalytic effects on x values is mainly ascribed to the variation in relative amounts of $\text{Co}^{4+}/\text{Co}^{3+}$

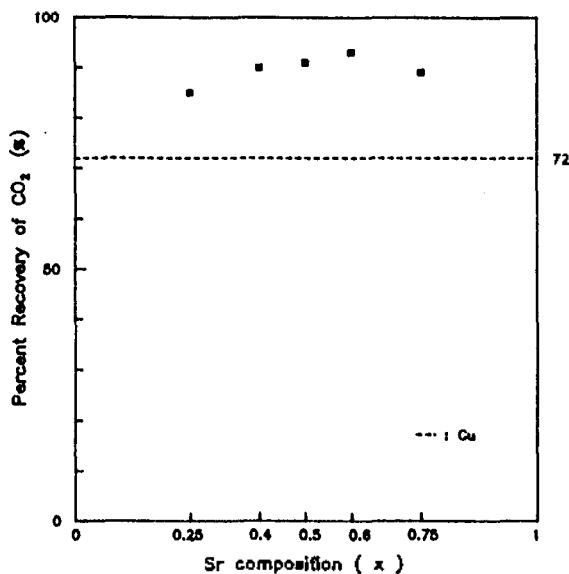


Figure 4. A Plot of percent recovery of CO₂ vs. x -value for the system of Nd_{1-x}Sr_xCoO₃ at fixed condition (total pressure of 30 torr and current of 5 mA).

and oxygen vacancies which affect conductivity as well as capability of oxidation. Namely, oxygen vacancies are created with O₂ desorption from the surface of catalysts which have unstable Co⁴⁺ changed into Co³⁺ by providing an electron. The amounts of oxygen vacancies proportional to x values make the diffusion of lattice oxygen easy. Therefore, both of the conductivity and catalytic effects tend to be increased by substitution of Sr²⁺, in general. However, if the substitution of Sr²⁺, x is larger than 0.6, both of them are decreased slightly⁷. This may be partially due to the reduction of reactivity on the surface by over-produced oxygen vacancy or the

slower reoxidation step in redox cycle of the catalyst.

As shown in the result, the amount of the CO₂ recombination in the catalytic electrode is increased in the order of 0.60 > 0.75 > 0.50 > 0.40 > 0.25 for x value. In addition, it has a close dependence on the current and the total pressure. When pressure was increased and current was decreased, it was increased. Therefore, Nd_{1-x}Sr_xCoO₃ series can be a good candidate as a catalytic cathode of a sealed-off CO₂ laser.

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Temperature Dependence of Carbon-13 Shieldings as a Probe for Conformational Equilibria

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The temperature dependence of C-13 chemical shifts are observed for the cyclooctanone arylhydrazones. The temperature-dependent chemical shifts for these derivatives are explained by postulating the existence of two equilibrating structures. In addition, the assignment between the ¹³C signals of methylene carbon pairs can be done by application of the γ -substituent effect.

Introduction

The utility of ¹³C-NMR spectra for structure studies is well established.¹ The temperature dependence of chemical shifts on the various nuclei have been known for some time, but the use of the effect with ¹³C data is relatively recent.²

It was once thought that the temperature dependence of chemical shifts could indicate the presence of an equilibrium in which the populations of different structures changed with temperature.^{3,4} However, Lambert reported a study in which he could see the temperature dependence of ¹³C chemical shifts to confirm the presence of both chair and twist-boat