CHEMISTRY LETTERS, pp. 1137-1140, 1977. Published by the Chemical Society of Japan

ELECTROCATALYTIC BEHAVIOR OF TETRASULFONATED METAL PHTHALOCYANINES IN THE REDUCTION OF CARBON DIOXIDE

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In the electroreduction of carbon dioxide, catalytic activities of the tetrasulfonated metal phthalocyanines(MeTSP) homogeneously dissolved in the Clark-Lubs buffer solutions were investigated by the measurements of current- and capacitance-potential curves. It was found that CoTSP and NiTSP were active but not CuTSP and FeTSP.

1. Introduction

As far as we surveyed, electrocatalytic activities of phthalocyanines for the reduction of CO_2 have not been investigated except for the study of Meshitsuka et al.[1] and much more investigations are necessary to obtain excellent catalysts. This paper describes an experimental study of the electrocatalytic activities of metal 4,4',4'',4'''-tetrasulfonated phthalocyanines(MeTSP) dissolved homogeneously in the solution, for the reduction of CO_2.

2. Experimental

The MeTSPs were prepared as described in Lits.(1) and (2). CO_2 gas was purified by passing through the hot finely devided copper activated by passing H_2 gas in advance, and then through a wash bottle containing an acidic solution of 0.1M vanadous sulfate and amalgamated zinc granules.

The reduction current and differential capacitance were measured under the potential sweep in a hard glass cell of conventional design having two compartments separated by a glass filter. The temperture was in all cases close to 2 °C, except for the experiments specially conducted to detect the temperature dependence of the current. Differential capacitance was obtained with a lock-in amplifier at 10 kHz. The test electrode consisted of an amalgamated platinum plate, the area of which was approximately 0.11 cm^2. A spiral of Pt wire served as the counter electrode. The reference electrode was a saturated calomel electrode which was connected to the cathode compartment through a salt bridge. Electrolytic solutions were Clark-Lubs buffer solutions prepared from triply distilled water and reagent grade chemicals.

3. Results and Discussion

3.1 Current-potential curves

The current-potential curves obtained in the solutions containing CoTSP or NiTSP as well as in the solution without MeTSP are shown in Fig.1. A distinct peak appeared in the solution with CoTSP or NiTSP under CO_2 bubbling. Such a peak was not observed for CuTSP or FeTSP. The peak current I_p increased with decreasing temperatures. The temperature dependence of I_p corresponded to that of the solubilities of CO_2 in the solution. The addition of Na_2CO_3 or $NaHCO_3$ into the solution had no effect on the current in N_2 atmosphere. I_p depended slightly on the concentration of MeTSP less than 4×10^{-4}M. These facts may indicate that the current peak is due to the electroreduction of CO_2 molecules catalysed by MeTSP. The value of I_p was not reproducible

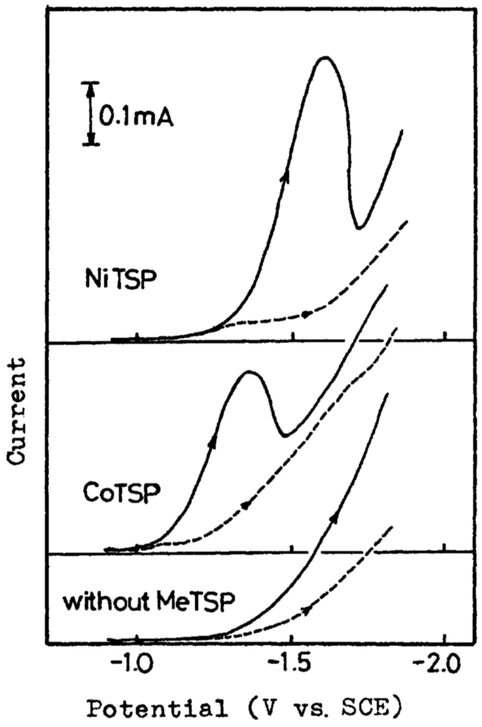

Fig.1. Cathodic current-potential curves obtained in the solutions (pH,7.0) of 5×10^{-4}M MeTSP; solid line, CO_2 bubbling; dotted line, N_2 bubbling; sweep rate, 110 mV/s.

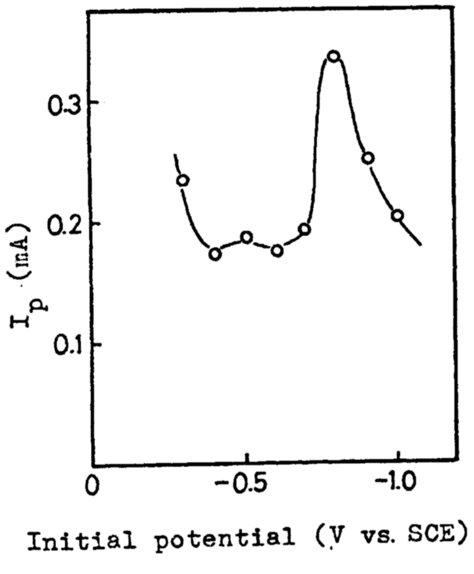

Fig.2. Effect of the initial potential on I_p; pH, 8.5; NiTSP, 5×10^{-4}M; sweep rate, 110 mV/s; holding time, 10 min.

unless the initial conditions of the potential sweep were always kept in the same states for each measurement. It depended on the position of the initial potential as shown in Fig.2 and also on the holding time at the initial potential. The holding time necessary for I_p to reach its maximum values was about 30 to 40 minutes and it tended to be shorter by stirring the solution. However, I_p was not influenced by the stirring of the solution under the potential sweep and almost disappeared by repeating the potential sweep four or five times.

NiTSP or CoTSP has two irreversible reduction waves in the current-potential curves$^{3)}$; the first wave appears at about -0.8 V vs. SCE and corresponds to the formation of monoanions and the second one at -1.2 V vs. SCE corresponds to the formation of dianions. It is noteworthy that the initial potential giving a maximum value of I_p (Fig.2) and the reduction potential of CO_2 (Fig.1) approximately correspond to these first and second reduction waves of MeTSP respectively. These facts may indicate that the reduction process of CO_2 consists of two steps. The first step which is most remarkably accelerated at around -0.8 V is the adsorption of CO_2 forming a complex with MeTSP and the second step is the electroreduction of the adsorbed complex at around -1.2 V.

3.2 Differential capacitance-potential curves

Two steps mechanism assumed from the current-potential curves may be ascertained by means of the capacitance measurements. Fig.3 shows a behavior of the interfacial differential capacitance measured under the potential sweep. A peak was observed at around -0.8 V which is the potential discussed above. Floviani and Fachinetti$^{4)}$ reported that Co(I)(salen)Na complex which was produced by one electron reduction of the corresponding cobalt(II) compound with sodium metal acted as a reversible CO_2 carrier. Therefore, also in our study, MeTSP which is produced at around

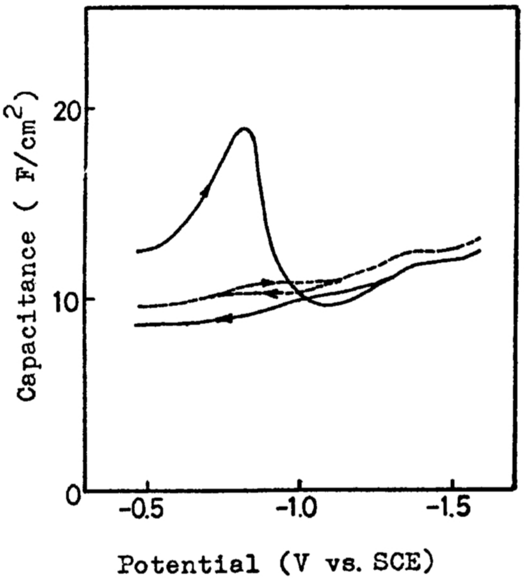

Fig.3. Differential capacitance obtained at 10 kHz under the potential sweep; NiTSP, 5×10^{-4}M; sweep rate, 22 mV/s; pH, 8.5; solid line, CO_2 bubbling; dotted line, N_2 bubbling

-0.8 V tends to be coordinated by CO_2 and to form CO_2-MeTSP complexes easily. Similar capacitance peak was observed at CoTSP but not CuTSP and FeTSP, which may indicate that the peak is concerned with the catalytic activities. However, the physical meaning of the capacitance peak is not still clear and the more detailed mechanism can not be discussed here.

The catalytic activities of metal phthalocyanines evaporated onto a metal lead (MeP-cathode) was also investigated. This cathode was active in the solution containing TEAP but not in the Clark-Lubs buffer solution, and it was found that MeTSP was much more active than MeP-cathode.

4. Conclusion

We found that CoTSP and NiTSP **served** as the active catalysts for the electroreduction of CO_2 in aqueous solutions. The overpotential for CO_2 reduction reduced about 0.2 to 0.4 V at 1 mA/cm^2 by the addition of MeTSP. It was considered that the reduction process consists of two steps; formation of CO_2 complex on the electrode and the electron transfer from the electrode to CO_2 through MeTSP. Investigation of the reduction products and the more detailed mechanism is now under way.

Acknowledgement

We are pleased to acknowledge the considerable assistance of M.Sato, M.Hattori, T.Kamigaki and N.Watanabe.

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(Received July 19, 1977)