

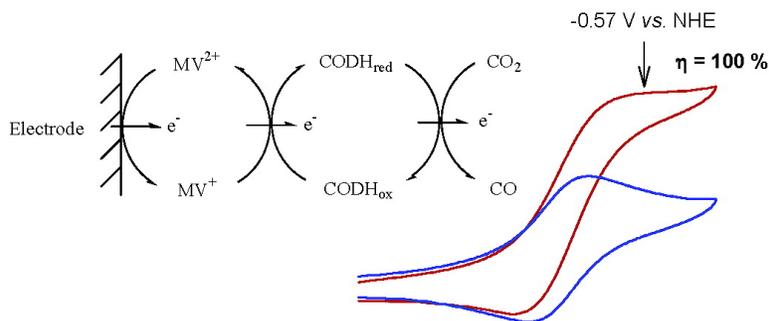
Communication

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Highly Selective Electrocatalytic Conversion of CO₂ to CO at -0.57 V (NHE) by Carbon Monoxide Dehydrogenase from *Moorella thermoacetica*

Woonsup Shin,* Sang Hee Lee, Jun Won Shin, Sang Phil Lee, and Yousung Kim

Department of Chemistry, Sogang University, Seoul 121-742, Korea

Received July 18, 2003; E-mail: shinws@sogang.ac.kr

We report here that carbon monoxide dehydrogenase (CODH) is a very efficient enzyme for the selective conversion of carbon dioxide to carbon monoxide, exhibiting almost no overpotential. Current efficiency is ~100% upon electrolysis at -0.57 V vs NHE in a 0.1 M phosphate buffer (pH 6.3). Carbon dioxide is the most abundant C₁ compound, and therefore, its conversion to more useful chemicals is important in recycling carbon species. It is also a major greenhouse gas, and its removal or conversion to other chemicals is extensively studied recently.¹ Since CO₂ is the most stable and the most oxidized state of carbon, the transformation of CO₂ to other compounds is fundamentally an energy-requiring reduction process. In addition, direct electrochemical reduction of CO₂ needs at least 1–2 V of overpotential. Therefore, an effective catalyst is essential for this process to overcome the activation barrier. A number of transition metal complexes² and a few enzymes³ have been investigated for this purpose but further work is required to develop efficient catalytic systems in terms of overpotential and selectivity.

CODH⁴ from *Moorella thermoacetica* (formerly *Clostridium thermoaceticum*) is a Ni- and Fe-containing metalloenzyme which catalyzes two types of reactions: the reversible oxidation of CO to CO₂ and the synthesis of acetyl-CoA. CODH has an α₂β₂ quaternary structure with metal ions organized into four types of clusters called A, B, C, and D. The A-cluster is responsible for the acetyl-CoA synthesis, and the C-cluster is responsible for CO₂/CO chemistry.⁵ Recently, the structure of this enzyme has been solved to 2.2 Å resolution⁶ and provides details on the arrangement of metal centers. Also, extensive spectroscopic studies have been done to elucidate the structure and function relationship of the enzyme.^{5,7} There was a preliminary investigation of CODH converting CO₂ to CO electrochemically,^{7d} but no systematic study has been done from the standpoint of electrocatalytic reduction of CO₂.

CODH⁸ did not communicate electrons directly with the electrode so an electron-transfer mediator, methyl viologen, was essential to deliver electrons to its redox centers. The reduced CODH converted carbon dioxide to carbon monoxide selectively. The electrocatalytic reduction scheme is shown below (Scheme 1).

Scheme 1. Electrocatalytic Reduction of CO₂ by CODH

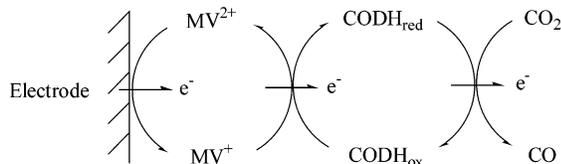


Figure 1a is a cyclic voltammogram of methyl viologen (MV) showing a typical reversible wave of MV^{2+/+} redox reaction at E^{o'} = -0.44 V vs NHE⁹ under nitrogen atmosphere. The voltammogram shape was little affected when the solution was saturated with CO₂. Upon adding CODH to the CO₂-saturated solution, we found that the current around the -0.5 to -0.6 V region increased

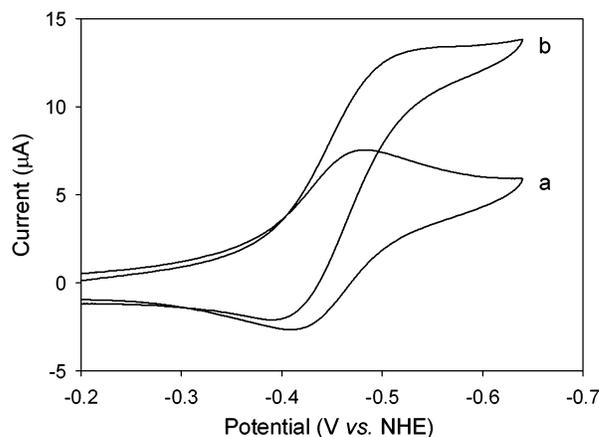


Figure 1. Cyclic voltammograms of (a) 1.0 mM MV²⁺ in 0.1 M phosphate buffer (pH = 7.0) and (b) 1.0 mM MV²⁺ containing 1 atm CO₂-saturated 0.1 M phosphate buffer (pH = 6.3) with 0.5 mg/mL of CODH at 50 °C. Glassy carbon disk (3 mm diameter) is used for working electrode, and scan rate is 10 mV/sec.

dramatically (Figure 1b). This is attributed to the catalytic reduction of CO₂ by CODH. Without CODH, the CO₂ reduction current was not observed in this potential range because the overpotential of the direct CO₂ reduction on the electrode is too large.

To analyze the reduced products and to estimate the current efficiency, the CO₂-saturated solution was electrolyzed at -0.57 V in the presence of CODH. Charge consumption and the amount of reaction products produced were followed during the electrolysis. The electrochemical cell was made of two gastight compartments divided by a Nafion 117 membrane. The working electrode compartment contained 3.0 mL of test solution with 12.0 mL of gas space. Gas sampling was done through a rubber septum on the gas-sampling port, and the inside pressure was adjusted by injecting the same volume of CO₂ gas before sampling. The dilution effect of the gaseous product was included in calculating the amount of the product. Results are shown in Figure 2. Carbon monoxide was the sole product, and no other gaseous or liquid products were detected by GC or LC. The current efficiency in every sampling point was in the range of 95–100%.

Since the thermodynamic CO₂/CO redox potential is -0.48 V at pH = 6.3,¹ the selective conversion of CO₂ to CO is achieved at less than 100 mV of its thermodynamic potential. This result indicates that CODH is the most efficient electrocatalyst of CO₂ reduction.^{1,2} Apart from this enzyme, the best known catalyst in aqueous solution is Ni cyclam²⁺ which can convert CO₂ to CO at -1.0 V vs NHE at pH 5.0.^{2c,d} The extremely low overpotential exhibited by CODH undoubtedly arises from the novel structure and the redox properties of C-cluster which nature developed for optimal CO₂ reduction. The C-cluster is known to have four different redox states (C_{ox}, C_{red1}, C_{int}, C_{red2}), and C_{red1}-to-C_{red2} state conversion, with E^{o'} = -0.52 V at pH 7.0,^{5a,7j} is thought to be

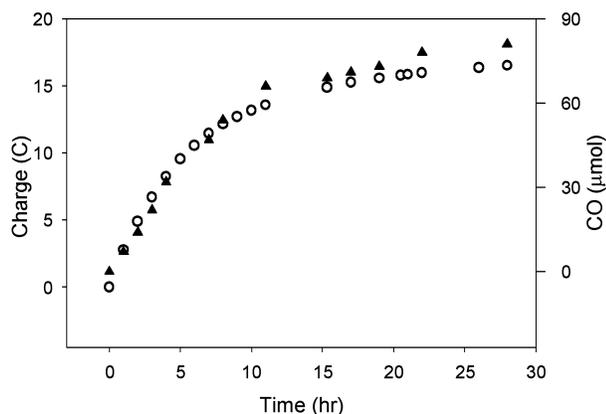


Figure 2. Electrolysis of CO₂ at -0.57 V vs NHE in the presence of 0.50 mg/mL of CODH and 1.0 mM MV²⁺ in 1 atm CO₂-saturated 0.1 M phosphate buffer (pH = 6.3) at gold flag electrode (16 × 6 mm) at room temperature. (○) Accumulated charge; (▲) CO production.

involved in CO₂ reduction.^{5,7,10} This potential is very close to -0.512 V of CO₂/CO redox potential at the same pH,¹ consistent with the reversible catalytic behavior of the enzyme and the low overpotential demonstrated here. Similar redox potential “matching” the redox potential of the substrate/product couple by nature is well-known.¹¹ For example, laccase, which is a well-known enzyme for four-electron reduction of O₂ to water, has a redox potential of $+0.43$ to $+0.79$ V for its copper center, depending on the source of the enzyme.¹² The redox potential of O₂/H₂O is $+0.816$ V at pH 7.0.¹³

The turnover number (per C-cluster) calculated from initial 3 h electrolysis data is 700 h⁻¹, which is 1 order of magnitude higher than other reported cases: 32 h⁻¹ for Ni cyclam^{2c,d} and 20–40 h⁻¹ for Fe porphyrin.^{2e,f} The remarkable conversion rate of CO₂ by CODH may also be attributed to the novel structure of [Ni–Fe₄–S_{4–5}]-type C-cluster^{6,14} which has never been synthesized. The unique structure may enhance the binding of CO₂ and the electron transfer to the substrate. Moreover, the conversion rate reported here was not optimized, and it might be improved further by adjusting temperature, mediator concentration, CO₂ pressure, etc. It would also be interesting to compare the abilities of *M. thermoacetica* CODH to CODHs from other sources. The decrease in CO production rate upon electrolysis time (Figure 2) was found to come mainly from the loss of the enzyme activity. A similar activity loss under reducing conditions has already been reported for other enzymatic systems.³

The effect of solution pH was also examined, and the optimum was found at pH 6.3. CO₂ reduction is a proton-requiring process, and the rate increases as the pH decreases. However, the activity of CODH drops quickly with decreasing pH. The balance between these two factors affords pH optimum at pH 6.3. For example, the initial CO₂ reduction current was higher at pH 6.0 than at pH 6.3, but it became reversed after 1.5 h of electrolysis. Moreover, the current efficiency is only 60% at pH 6.0 and hydrogen evolved.

In summary, CODH is found to be an excellent catalyst for the electrochemical carbon dioxide reduction. It converts CO₂ selectively to CO with almost no overpotential.

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