Improvement of CO_2 reduction catalytic activity of biocatalyst by artificial co-enzyme

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1. Introduction

Formate dehydrogenase (FDH) is an attractive biocatalyst for the CO_2 reduction, because CO_2 is converted to HCOOH by FDH at expense of NADH as reductive co-enzyme, under ambient conditions, in neutral aqueous solution. But FDH mainly catalyzes the conversion of HCOOH to CO_2, concented with the reduction of NAD^+ to NADH. Thus, a method to suppress the FDH catalytic activity of the oxidation of HCOOH to CO_2 has been needed for a long time. To solve this problem, reduced form of viologen derivatives, methylviologen and diquat, were used as artificial co-enzymes for FDH in the conversion of CO_2 to HCOOH and the CO_2 reduction catalytic efficiency of FDH was improved by using those artificial co-enzymes in place of NADH[1,2]. In addition, the use of viologen derivatives effectively suppressed the reverse reaction by FDH.

To improve the CO_2 reduction catalytic activity of FDH, viologen derivatives with different ionic group (amino or carboxyl) shown in Fig. 1 were synthesized as novel artificial co-enzymes for FDH.

2. Experiment

To clarify the effect of ionic group in viologen derivative on the CO_2 reduction to HCOOH with FDH, kinetic studies were carried out. For enzyme kinetics analysis, CO_2 - HCOOH conversion with dithionite-reduced viologen derivative with ionic group and FDH was carried out by following condition. The sample solution was consisted of viologen derivative, sodium dithionite (4 mM) and FDH (6.4 μM) in CO_2 saturated 1 mM sodium pyrophosphate buffer (pH 7.4).

3. Result and discussion

Each viologen derivative with ionic group acted as an artidficial co-enyzme for FDH in the conversion of CO_2 to HCOOH. Table 1 shows the obtained parameters from the kinetics analysis. The catalytic efficiency value (k_{cat}/K_m) of the reduced form of 1,1'-diaminoethyl-4,4'-bipyridinium salt (DA) was the largest in other viologen derivatives. On the other hand, the k_{cat}/K_m value of the reduced form of 1,1'-dicarboxymethyl-4,4'-bipyridinium salt (DC) was the smallest in others. These results indicated that CO_2 reduction for k_{cat} / K_m value was influenced by ionic group on the viologen derivative and the CO_2 reduction catalytic activity was improved by using viologen derivative with amino group.

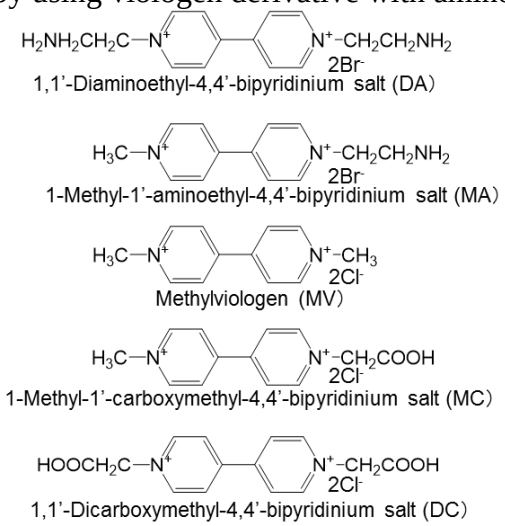

Fig. 1 Chemical structures of artificial co-enzyme with ionic group.

Table 1. Kinetic parameters for CO_2 to HCOOH conversion with dithionite-reduced artificial co-enzyme and FDH

	K_m μM	k_{cat} min^{-1}	k_{cat}/K_m $\mu M^{-1}\cdot min^{-1}$
DA	17	4.3	0.25
MA	118	2.3	1.9×10^{-2}
MV	212	1.9	9.0×10^{-3}
MC	292	1.5	5.1×10^{-3}
DC	371	0.3	9.3×10^{-4}

(K_m: Michaelis constant, k_{cat}: turn over number, k_{cat}/K_m: CO_2 reduction catalytic efficiency)

REFERENCES

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