Table I. Resonance Raman Frequencies and Relative Intensities of the Blue Copper Proteins between 300 and 500 cm^{-1}

plastocyanin		azurin		stellacyanin	
ν, cm^{-1}	I_{rel}[a]	ν, cm^{-1}	I_{rel}[a]	ν, cm^{-1}	I_{rel}[a]
343	0.08	348	0.04	334	0.06
377	0.7	373	0.4	348	0.6
387	0.5	400	0.4, sh	359	0.3
393	0.4				
407	0.5	409	1.0	373	0.2
425	1.0	428	0.5	386	1.0
442	0.6	441	0.1	407	0.2
		455	0.07		
				424	0.14
480	0.1	474	0.04	444	0.08
491	0.1	492	0.03	492	0.06

[a] I_{rel} of the strongest peak in each spectrum is taken as 1.0; all other peak intensities are given as fractions of the strongest peak.

been identified crystallographically as one cysteine sulfur, one methionine sulfur, and nitrogens from two histidine imidazole residues.[7,8] While a stretching frequency near 400 cm^{-1} is reasonable for a RS^--Cu^{2+} bond,[9] it is unprecedentedly high for a M^{2+}–N(imidazole) bond. The latter typically have stretching frequencies near 250 cm^{-1}.[10–12] The Cu–S(methionine) bond in plastocyanin appears from the crystal structure to be exceptionally long (~2.8 vs. ~2.3 Å for typical Cu^{2+}–S(thioether) bonds).[8,13] Considering that normal Cu^{2+}–S(thioether) stretching frequencies are near 270 cm^{-1},[9,14] it appears inconceivable that the freqnency due to the long Cu–S(methionine) bond in the proteins could be near 400 cm^{-1}.

From the foregoing it appears that only one of the metal–ligand stretching modes of the blue copper chromophore is actually expected to be near 400 cm^{-1}. Yet Table I shows that nine modes in this frequency range have intensities within approximately an order of magnitude of one another. Clearly, some of these modes must be other than copper–ligand stretches. We may discard LCuL, CuSC, and CuNC deformations as reasonable possibilities at these frequencies. We are left with vibrations of the ligands thermselves. These include the C–S–C angle bend of methionine, the S–C–C bend and α-carbon deformations of cysteine, the C–S stretches of cysteine and methionine, and imdazole ring deformations as motions that might plausibly be resonance enhanced. The C–S stretches are expected[9,14] and observed[5] (for cysteine) near 750 cm^{-1}. Considering the long Cu–S(methionine) bond and the belief[6] that methionine charge transfer contributes insignificantly to the electronic absorbance of the blue copper chromophore, observation of the C–S–C bend of methionine appears unlikely. It is reasonable for one of the modes to be the S–C–C bend. Resonance enhancement of two or three cysteine α-carbon deformations, while less likely, cannot be excluded. The most reasonable assignment for the remaining modes is as histidine imidazole ring deformations. While the IR and Raman spectra of solid imidazole do not show peaks in the 300–500-cm^{-1} region,[15,16] IR spectra of the partially deuterated sample[16] exhibit frequencies that, allowing for the maximum deuterium shift, suggest that normal imidazole has internal motions near 400 cm^{-1}. Further, preliminary results[17] of low-temperature Raman studies of histidine show peaks in the 300–500-cm^{-1} region. It is noted that previous normal mode analyses of imidazole[15,16] do not take into account the existence of modes in this region and that, in any case, imidazole itself may be an inadequate vibrational model for the alkyl-substituted imidazole represented by histidine.

If imidazole ring deformations are resonance enhanced in these proteins, it is clear that these deformation motions may mix with the M–L stretches. Indeed, one explanation of the "anomalously high copper–imidazole stretching frequencies" is that none of the modes near 400 cm^{-1} need be Cu–N stretches at all, but could instead be highly mixed motions involving the Cu–S stretch and internal ligand modes including imidazole ring deformations. We suggest that the Cu–N stretches appear, as they do in model systems,[11,12] in the 200–300-cm^{-1} region (see Figures 1 and 2). In agreement with earlier work[2–5] we assign the Cu–S(cys) stretch either as one of or distributed among the strong peaks near 400 cm^{-1}.

The foregoing assignment provides a reasonable mechanism for significant variability of the frequencies of analogous RR modes from one protein to another. The extent of the interaction between the Cu–L stretches and the ligand deformations should be very dependent upon the geometry of the CuL_4 core and also the orientations of the imidazole rings and cysteine dihedral angles with respect to the Cu–L bonds. The protein structure controls these structural parameters and therefore may control the magnitude of the stretch–deformation interactions.

We note the remarkably similar appearance of the spectra of plastocyanin and stellacyanin between 300 and 500 cm^{-1} (Figure 2). Each of the peaks of stellacyanin is approximately 30 cm^{-1} lower in frequency than the corresponding feature in plastocyanin, and stellacyanin exhibits an extra feature at 424 cm^{-1}. This similarity is not evident in the room-temperature solution RR spectra.[2–4]

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Metal Electrodes Bonded on Solid Polymer Electrolytes: Platinum Bonded on Solid Polymer Electrolyte for Electrooxidation of Methanol in Perchloric Acid Solution

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The catalytic activity of a platinum electrode bonded to a solid polymer electrolyte (SPE) membrane with either cation- or anion-exchange properties was examined for electrooxidation of methanol. The stability of the catalytic activity was found to be much better than that of a bulk Pt electrode.

Recently, various SPE-coated electrodes were prepared, and their chemical properties were investigated.[1,2] We prepared platinum directly bonded onto an SPE membrane (Pt-SPE). The procedure was as follows.[3] The membrane was swelled in boiling water for 0.5–2 h and then mounted on a vessel so that one face of the membrane contacted a 0.01–0.02 M H_2PtCl_6 aqueous solution and the other face contacted a 0.1–1.5 M $NaBH_4$ aqueous alkaline solution. The reducing agent, borohydride, was allowed

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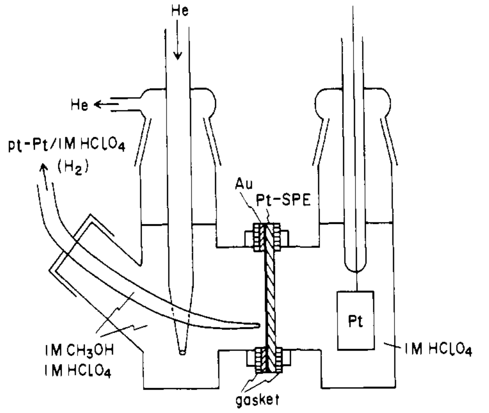

Figure 1. Electrolytic cell for methanol electrooxidation. In the compartment on the platinum side of Pt–SPE, a solution of 1 M CH_3OH + 1 M $HClO_4$ was introduced and deaerated with He gas. For contact with the lead wire, Au foil was inserted between Pt–SPE and the left-hand side gasket made of Teflon and silicone rubber (Uni-sheet, NRK). The reference electrode, platinized Pt, in H_2 saturated 1 M $HClO_4$ was connected from the platinum side of Pt–SPE through a Luggin capillary. In the other compartment, a counterelectrode (Pt gauze) was inserted in 1 M $HClO_4$. When the test electrode in the left-hand side compartment was platinized platinum, Pt–SPE was replaced with a plain SPE(Nafion).

to penetrate the SPE to reduce Pt ions to Pt metal at the face of the membrane. The membranes used were Nafion[4] and Neosepta.[5] The formation of Pt metal took place more easily on Neosepta than on Nafion. The amount of the platinum per unit apparent area of the membrane was 4–8 mg/cm^2.

An electrolytic cell with two compartments made of glass, connected to a reference electrode cell, shown in Figure 1, was used. The test electrode (Pt–SPE) was inserted between the two compartments.

To determine the surface features of the Pt–SPE, we compared the electrochemical adsorption–desorption processes of hydrogen and oxygen on Pt–SPE with those on Pt. The processes were nearly identical on both Pt electrodes. Thus the platinum of Pt–SPE was nearly identical with bulk Pt. This indicates that the adsorption–desorption processes on the Pt–SPE are not largely affected by modification of the platinum environment by the SPE.

However, for the electrooxidation of methanol a cyclic current-potential (i–E) curve on Pt–SPE(Nafion) was very different from that on Pt,[6] as shown in Figure 2.[7] The current did not decrease at 0.8–0.9 V on Pt–SPE with an increase of potential and kept increasing up to 1.2 V. This feature also appeared in the i–E of Pt–SPE(Neosepta).

It is known that a Pt electrode, which exhibits a high catalytic activity just after anodic activation, does not maintain this activity during long-term polarization of methanol oxidation.[8] The time dependence of the polarization current density on Pt–SPE's (log i vs. τ) was compared with that on a platinized platinum (pt–Pt) at 0.6 V vs. RHE, as shown in Figure 3. After a long period of polarization, the catalytic activity of the platinum remained high whether bonded on a cation- or on an anion-exchange membrane; the order of the catalytic activity was approximately 20:10:1 for Pt–SPE(Nafion):Pt–SPE(Neosepta):pt–Pt after 20 h of polarization.

The electrostatic potential at the interface (Donnan potential) is opposite in sign for cation- and anion-exchange membranes.

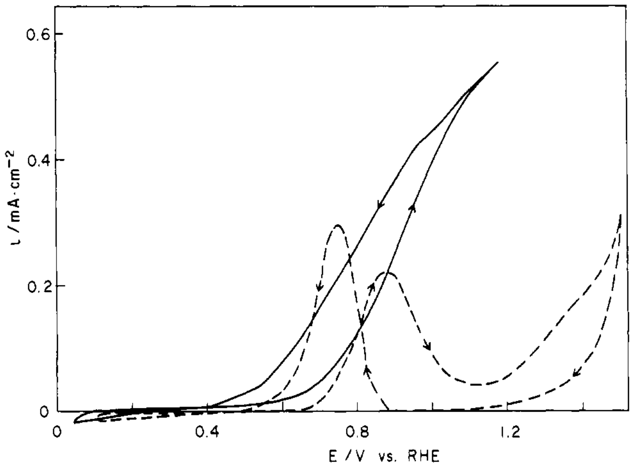

Figure 2. Cyclic current-potential curves in 1 M CH_3OH + 1 M $HClO_4$. Potentials are with respect to a reversible hydrogen electrode (RHE). The solid curve is for Pt–SPE(Nafion) at a sweep rate of 25 mV/s and the dotted curve is for a Pt-wire at a sweep rate of 20 mV/s. The roughness factor of the platinum of Pt–SPE was 83, estimated from the amount of adsorbed hydrogen.

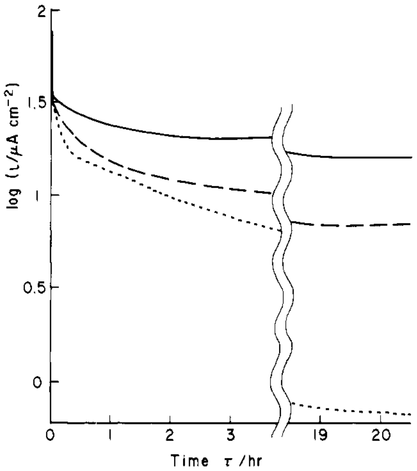

Figure 3. Time course of polarization of 0.6 V vs. RHE. The solid curve is for Pt–SPE(Nafion), the dashed curve for Pt–SPE(Neosepta), and the dotted curve for pt–Pt. The roughness factors were 630 for both Pt–SPE's and 350 for pt–Pt.

Thus, a simple electrostatic interaction does not produce the difference of the i–E curves and the appearance of high durability of the catalytic action. Rather, the catalytic action of the SPE matrix is the most likely source of these findings. Since in the SPE matrix the states of the ions and solvent are different from their states in the bulk solution,[9] the electrode bonded on the SPE may change its electrocatalytic properties from the electrode in the solution. It has been proposed that the occurrence of possible redox coupling of platinum in different oxidation states is essential for the durability of catalytic activity of Pt–Sn oxide.[8] Thus, a ratio of platinum ions to Pt^0 on the surface of the electrode was measured by XPS; the ratio on Pt–SPE(Nafion) was 1.8 times higher than that on Pt metal.[10] This suggests that the matrix of the SPE acts to stabilize Pt ions on the Pt–SPE to maintain the occurrence of the redox coupling of platinums.

The electrolysis of gaseous species, e.g., hydrogen and oxygen, was demonstrated to be possible without the electrolytic solution on the electrode side of Pt–SPE.[11]

Registry No. CH_3OH, 67-56-1; $HClO_4$, 7601-90-3; Nafion, 39464-59-0; Neosepta, 52350-42-2.

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(5) Product of Tokuyama Soda. Neosepta ACH-45T, an anion-exchange membrane of a quaternary ammonium polymer, was used.

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