March, 1993] © *1993 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,**66**, 963—965(1993)* 963

A Major Factor Controlling the SERS Band Intensity of Pyridine Adsorbed on a Silver Electrode

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(Received October 26, 1992)

Synopsis. SERS intensity of pyridine has been examined as a function of the amount of charge necessary for the formation of Ag atom during the ORC procedure in each of several electrolytes. The amount of the reduction charge was controlled so as to hold a constant value of around 50 mC cm^{-2}. Although the efficiency of charge recovery in the reduction process with nonhalide ion was very poor compared with chloride ion, intense SERS bands as large as in the case of chloride ion were found even in the case of nonhalide ion.

For the SERS spectra in the electrochemical system, the oxidation–reduction cycle (ORC) procedure is very important to obtain sufficiently enhanced intensity of the SERS band.[1—5] The supporting electrolyte so far mostly used for the SERS measurement is alkali halide, which has been suggested as playing an important role in the formation of the surface roughness and the SERS active site.[6—8]

Jeanmaire and Van Duyne,[2] and Pettinger and Wetzel[6] reported that the SERS intensity of the pyridine adsorbed on a silver electrode in the supporting electrolyte containing halide ion was much larger than that containing nonhalide ion such as $\mathrm{ClO_4^-}$, $\mathrm{NO_3^-}$, and $\mathrm{SO_4^{2-}}$ by about two orders of magnitude. Gao et al. reported that the decrease in the pyridine SERS intensity on a silver electrode upon substitution of $\mathrm{Cl^-}$ by $\mathrm{ClO_4^-}$ can be attributed to the involvement of a chloride-pyridine "surface complex".[9] For the SERS studies on a silver electrode, electrolyte solution of nonhalide anions have scarcely been examined as compared with halide anions[10—12]

Several causes have been proposed on the SERS origins where the amount of active site is included. With regard to the amount of active site, however, few quantitative studies seem to have been carried out. Hence, it is worthwhile to examine the relationship between the amount of the reduced Ag atom which is regarded to form the active site and the ORC conditions for obtaining the intense SERS spectrum in various types of electrolyte in the presence and in absence of halide anion.

In the present study, we controlled the amount of electric charge necessary to reduce $\mathrm{Ag^+}$ ion to form fresh Ag atom for each of nonhalide supporting electrolyte solution during the ORC. It was found that the strong SERS band intensity for adsorbed pyridine can be obtained when the amount of reduced Ag atom during the ORC is sufficient in any electrolyte irrespective of the species of anion.

Experimental

For the test electrode, a polycrystalline cylindrical silver rod of 4 mm diameter was tightly inserted into a Teflon cylinder which was mounted in an electrochemical glass-cell for SERS experiments. Supporting electrolytes tested were 0.1 M KCl, $\mathrm{KClO_4}$, $\mathrm{KNO_3}$, and $\mathrm{Na_2SO_4}$ (1M=1 mol $\mathrm{dm^{-3}}$), which were prepared by dissolving reagent grade of these salts and pyridine in triply distilled water. A series of measurements were performed under an identical condition except for the oxidation potential during the ORC. All measurements were carried out in solution of pH 7.7 at room temperature.

As a reference electrode, Ag/AgCl/sat. KCl electrode was used. In the case of nonhalide electrolyte, the reference electrode was separated from a supporting electrolyte solution by a salt bridge containing the supporting electrolyte of the same concentration.

Before the measurement of SERS, the electrode potential was set to a desired negative potential (SCE), then set to a positive potential and held for 3 s, and finally set back to the initial value, which was controlled by a computer. This double potential stepping procedure will hereinafter be called ORC. The ORC was always performed in the presence of 50 mM pyridine.

Raman spectra were measured with an instrument consisting of 750 mm Nalumi model 750Z-1200 double monochromater, an HPK 649S photomultiplier, and an ORTEC photon counting system. A JEOL He–Ne laser (632.8 nm, 50 mW) was used.

Results and Discussion

At first the usual ORC procedure was examined for a silver electrode in various electrolytes containing 0.1 M of each salt and 50 mM pyridine. This model ORC procedure is as follows: (1) the potential of the silver electrode is set at −0.4 V vs. SCE; then (2) stepped to +0.2 V for 3 s; and then (3) decreased to the initial value (−0.4 V) in the same manner. This procedure was applied for each electrolyte. The electric currents due to the oxidation and the reduction with nonhalide ion were found to be far less than those with halide ion under the same ORC conditions. These results are shown in Table 1.

A suitable potential range of the ORC for a silver electrode was chosen depending on the chemical nature of the electrolyte but the limit was set within the range of +0.8 V vs. SCE (oxidation) and −0.6 V (reduction). The oxidation potential of the silver electrode E_0, however, is strongly affected by the dissolved electrolyte, e.g., E_0 for $\mathrm{ClO_4^-}$-containing solution is at around +0.55

Table 1. Oxidation-Reduction Electrode Potential and Amount of the Electric Charge Transfer for Various Electrolytes

Electrolyte	E_{ox} (V)[a]	E_{red} (V)[b]	Q_{ox}(mC cm^{-2})[c]	Q_{red}(mC cm^{-2})[c]	$Q_{\mathrm{red}}/Q_{\mathrm{ox}}$
KCl	0.20	−0.4	48	47	0.98
Na_2SO_4	0.20	−0.4	<1	<1	—
	0.76	−0.4	75	40	0.53
KNO_3	0.20	−0.4	<1	<1	—
	0.76	−0.4	74	40	0.58
$KClO_4$	0.20	−0.4	<1	<1	—
	0.76	−0.4	83	43	0.52

a) Oxidation potential (vs. SCE), b) Reduction potential, c) Charge transfer of silver electrode (mC cm^{-2}).

V vs. SCE, which shifts to −0.02 V in Cl^--containing solution, whose features are schematically depicted in Fig. 1.

When we performed the model ORC in the above-stated potential range, we could obtain a substantial amount of freshly formed Ag atom in Cl^- solution while only a lesser amount would be available in NO_3^- solution, since only a very limited current would flow for Ag^+ formation (in addition to the diffusing of formed Ag^+ away from the electrode surface). Thus the amount of formation of Ag atom upon reduction would be strongly limited.

Therefore, for the case of nonhalide ion we controlled the amount of the reduction charge transferred during the ORC to be around 50 mC cm^{-2} by adjusting the ORC potential and time. A value of 50 mC cm^{-2} was adopted as an appropriate value by taking into consideration the results of Jeanmaier and Van Duyne[2] for the case of halide anion. The appropriate applied potentials and charges transferred during the ORC are also given in Table 1. Strong SERS band intensities of the ring skeletal modes of adsorbed pyridine appearing at 1008 and 1035 cm^{-1} could be observed for every case as shown in Fig. 2, where deposition of the amount of fresh Ag atom was kept nearly the same for all the electrolyte. The same magnitude of SERS intensity of pyridine could be obtained even for the electrolyte solution of ClO_4^-, NO_3^-, or SO_4^{2-} as that obtained for the

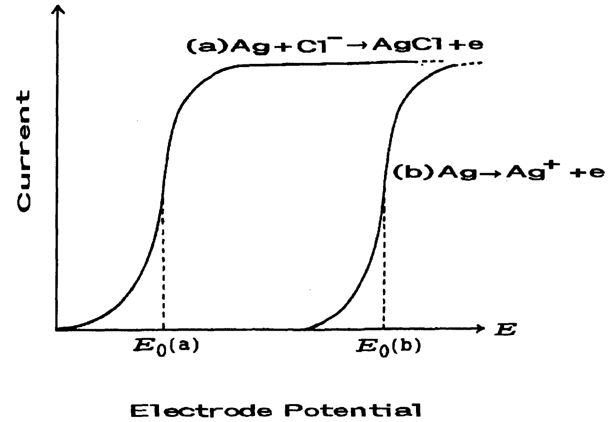

Fig. 1. Schematic current-potential curves of the oxidation process on a silver electrode, (a) in 0.1 M KCl aqueous electrolyte (the half wave potential=E_0 of reaction (a)), (b) in 0.1 M $KClO_4$ aqueous electrolyte.

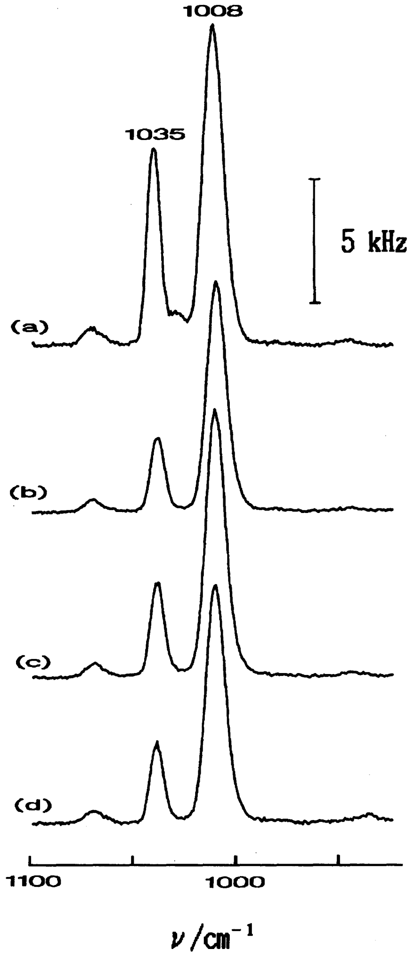

Fig. 2. SERS spectra of adsorbed pyridine on a silver electrode at −0.4 V vs. SCE immersed in 50 mM pyridine +0.1 M of each electrolyte solution; (a) KCl, (b) Na_2SO_4, (c) KNO_3, and (d) $KClO_4$. In all cases, the amount of charge reduced during the ORC was controlled to the extent of 50 mC cm^{-2}. The spectra were scanned at 0.7 cm^{-1} s^{-1} and the spectral slit width was 6 cm^{-1}.

Cl^- anion solution.

From the present results we have been able to prove that the strong intensity of SERS band due to adsorbed pyridine can always be obtained if the amount of freshly deposited Ag atom is sufficient in any electrolyte irrespective of the species of anion.

However, it has so far been suggested that the halide anion is effective to give rise to a strong SERS band.[2,6,9] The reason why the presence of any halide anion is effective to cause a strong SERS band is very obvious since halide catches Ag^+ formed during the ORC as an insoluble halide salts which can not diffuse away from the surface of Ag electrode. On the other hand, in the solution of nonhalide electrolyte there is no possibility of such an effective catch of Ag^+, and the amount of Ag^+ to be reduced is rapidly decreased with the lapse of time by the diffusing of formed Ag^+ away from the electrode surface into bulk, resulting in only a restricted amount of reduced Ag is formed during the fixed time period. Such a problem of low amount of depositing Ag in nonhalide solution has been solved in the present study.

Several reasons have been postulated as factors to causes SERS, i.e. surface morphology, surface roughness, and the interaction between pyridine and anions. Regarding the interaction between pyridine and anions, some complex of pyridine/silver/halide has been suggested as a cause of the SERS enhancement.[9] Such a halide complex mechanism, however, is unacceptable in the case where strong SERS band was still observed in nonhalide electrolyte as shown in Fig. 2. With these results the most reasonable explanation is as follows: In the present case the same amount of reduced Ag atom may form the similar surface morphology to each other irrespective of electrolyte. A constant amount of freshly deposited Ag atom during the ORC may form atomic scale roughness involved in the chemical enhancement[13—15] and at the same time may form macroroughness which yields the SPP enhancement,[1,16] both of which would be stabilized immediately by the adsorption of pyridine.[17] The adsorbing pyridine plays the most important role to maintain the activity of the SERS site.

Therefore, it is considered that the same strength of the SERS may be obtained by the same number of pyridine adsorbed on the SERS active site under the same magnitude of the enhancement to each other irrespective of electrolyte for each of the chemical and the SPP enhancements.

We thus found that a large SERS band intensity could successfully be obtained even without halide if we control the amount of charge recovery of Ag atom in the reduction process. These findings indicate that the amount of freshly deposited Ag atom which has just been formed by the reduction during the ORC is a major factor in the SERS enhancement.

The author wishes to express his gratitude to Professor Tsutomu Takamura of Rikkyo University for his useful discussions. He also wishes to thank Dr. Yasunari Ikezawa for helpful discussions and technical suggestions, and Professor Gene S. Lehman for his kindness in reading the original manuscript.

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