Thin-layer electrochemical resonance-Raman measurement for complex electrode reactions

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Resonance-Raman spectroscopy in conjugation with electrochemical measurements clarify that the complex voltammetric response of 2,3,5,6-tetrachloro-1,4-benzoquinone (TCQ) in the presence of Mg^{2+} is due to the further reduction of the intermediate ion pair, $Mg^{2+}\cdot TCQ^{\cdot -}$, to the dianion pair, $Mg^{2+}\cdot TCQ^{2-}$.

We have developed a thin-layer electrochemical resonance-Raman (TLERR) method to analyse electrode reactions. The RR measurement using a thin-layer spectroelectrochemical cell has an advantage in that the species only in the vicinity of the solution/electrode interface can be targeted, so that electrochemical or chemical reactions on the electrode surface can be directly observed. In the present paper, useful features of the TLERR method in analysing complex electrochemical reactions are presented.

In our previous paper, we studied the ion pair formation between 2,3,5,6-tetrachloro-1,4-benzoquinone (TCQ; chloranil) radical anion ($TCQ^{\cdot -}$) and Mg^{2+} by using a pulse electrolysis stopped-flow method, and clarified that the contact ion pair, $Mg^{2+}\cdot TCQ^{\cdot -}{}_2$, was formed in acetonitrile.[1] While the reaction in homogeneous solution is now clear, the complex electrochemical response has still to be understood. Fig. 1 shows the changes in cyclic voltammograms (CV) on the reduction of TCQ upon addition of Mg^{2+}. With increasing concentration of Mg^{2+}, the reversible peaks (P_1, P_2) gradually diminish and a new irreversible cathodic peak (P_3) appeared at a potential slightly positive relative to P_1.

To investigate this electrochemical reaction process in detail, we observed the Raman spectra in the vicinity of the electrode by using the TLERR method when the negative potential was applied to form $TCQ^{\cdot -}$.

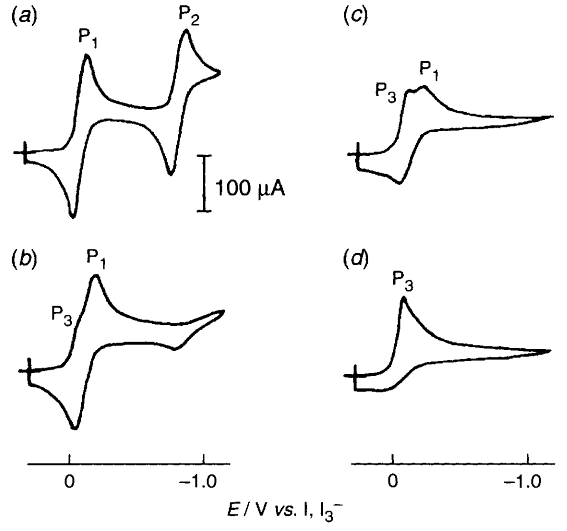

Fig. 1 Changes in cyclic voltammograms of TCQ in MeCN with the addition of Mg^{2+}. Scan rate, 100 mV s^{-1}. The solution was 5.0 mmol dm^{-3} TCQ and 0.10 mol dm^{-3} Bu_4NClO_4 in MeCN; Mg^{2+} was added by dissolving $Mg(ClO_4)_2$. [Mg^{2+}] (*a*) 0, (*b*) 1.0, (*c*) 2.0, (*d*) 3.0 mmol dm^{-3}.

The electrode used was a glassy carbon disk electrode (Tokai Carbon, GC-20; diameter 3.0 mm). The electrode surface was covered tightly with the quartz window of the cell (diameter 9.0 mm) to achieve the thin-layer conditions. When the cell was filled with a sample solution, the solution infiltrated onto the whole area of the glassy carbon electrode surface, as confirmed visually. Potentiostatic electrolysis was performed with a three-electrode system: a Pt wire counter-electrode was put around the working electrode, and a $Pt/(I^-,I_3^-)$ reference electrode was inserted close to the working electrode. In the Raman measurement, the electrochemical cell was set up so that its window faced the entrance slit of a spectrophotometer. The excitation Ar^+ laser line of 488.0 nm was used to irradiate the electrode surface from the side with an incident angle of 25° to the plane of the window. Two collection lenses and a holographic notch plus filter (Kaiser Optical System, Inc.) for removing the Rayleigh light were placed between the cell and the spectrophotometer. The detection system with a multichannel detector has been described previously.[2]

For species at low concentration levels as used in normal voltammetric measurements, resonance enhancement effect is necessary to obtain the Raman spectra in solution. In the case of $TCQ^{\cdot -}$, once $Mg^{2+}\cdot TCQ^{\cdot -}{}_2$ was formed in homogeneous MeCN solution, the absorption spectrum was drastically changed from free $TCQ^{\cdot -}$; the absorption maxima of free $TCQ^{\cdot -}$ and $Mg^{2+}\cdot TCQ^{\cdot -}{}_2$ are at 449 and 290 nm, respectively.[1] Hence, as a result of Raman measurement for free $TCQ^{\cdot -}$ and $Mg^{2+}\cdot TCQ^{\cdot -}{}_2$ solutions by excitation of 488.0 nm, the RR spectrum was observed only for free $TCQ^{\cdot -}$ owing to the resonance effect. The obtained RR spectrum was similar to that obtained by dissolving $K^+\cdot TCQ^{\cdot -}$ in acetone.[3]

To observe the ion-pair interactions between $TCQ^{\cdot -}$ and Mg^{2+} in the vicinity of the electrode surface, we carried out the TLERR measurement for a 5.0 mmol dm^{-3} TCQ solution in the presence of various concentrations of Mg^{2+} by stepping the applied potential from +0.5 to −0.5 V. Since the current response decreased over very short times (< 1 s), thin-layer conditions are assumed to be achieved in this cell. The Raman signal was observed for 3 min after the potential step, *i.e.* the measurement was carried out for the steady state of the electrode surface at a potential of −0.5 V.

Fig. 2(*a*) shows the Raman spectrum measured after the potential step for a solution of TCQ in the absence of Mg^{2+}. This spectrum is similar to the RR spectrum of free $TCQ^{\cdot -}$ measured in homogeneous solution. Next, we performed Raman measurements for TCQ solutions containing Mg^{2+}. Upon increasing the concentration of Mg^{2+}, the RR peaks of free $TCQ^{\cdot -}$ decreased as shown in Figs. 2(*b*) and (*c*). Thus, free $TCQ^{\cdot -}$ is assumed to diminish through ion-pair formation on the electrode surface as well as in homogeneous solution.

However, the decrease of free $TCQ^{\cdot -}$ during the ion-pair formation process as measured by the TLERR method was markedly different from previous results in homogeneous solution. Fig. 3 summarizes the changes in the RR signals depending on the molar ratio of [Mg^{2+}] : [TCQ] together with the previous results in homogeneous solution. In the previous measurement, in which the absorbance change was followed by mixing the solutions of Mg^{2+} and $TCQ^{\cdot -}$ after the quantitative electrolysis of TCQ, the ion pair formed was clearly determined to be $Mg^{2+}\cdot(TCQ^{\cdot -})_2$.[1] By contrast, the decrease of the intensity of RR bands depending on the molar ratio was quite different, so the Mg^{2+} : TCQ stoichiometry could be determined as 1 : 1.

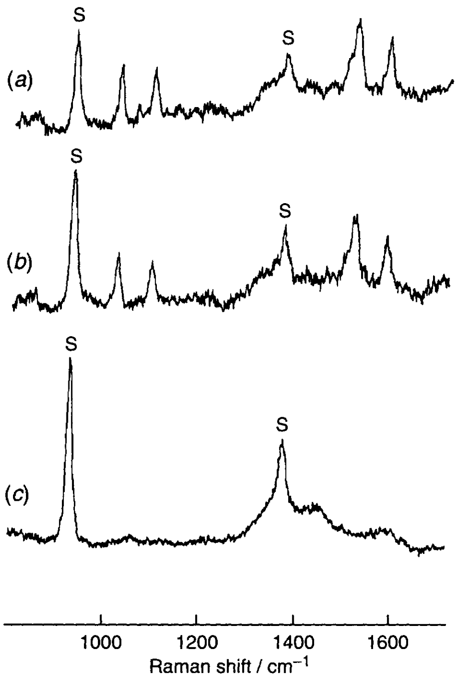

Fig. 2 Resonance-Raman spectra of electrolysed solutions containing TCQ and Mg^{2+} measured in thin-layer cell. The applied potential was stepped from +0.5 to −0.5 V. Total accumulation time of Raman signal was 5 s during 3 min after the potential step. The solution was 5.0 mmol dm^{-3} TCQ and 0.10 mol dm^{-3} Bu_4NClO_4 in MeCN; [Mg^{2+}] (*a*) 0, (*b*) 2.0, (*c*) 5.0 mmol dm^{-3}; S denotes the Raman band of the solvent.

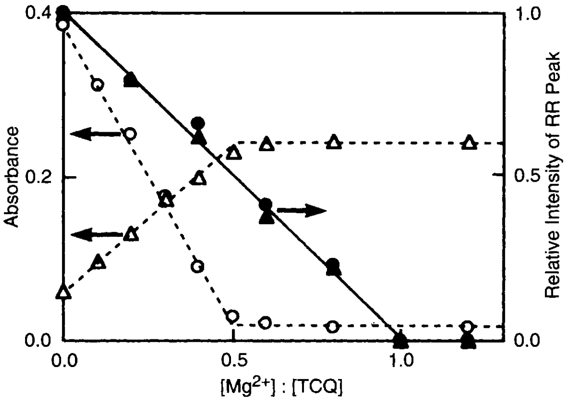

Fig. 3 Changes in intensity of RR peaks of $TCQ^{\cdot -}$ depending on the [Mg^{2+}] : [TCQ] ratio together with previous results in homogeneous solution. The Raman intensity was normalized using the solvent Raman band at 920 cm^{-1} and expressed as a relative value to the spectrum in the absence of Mg^{2+}. (▲) 1019, (●) 1086 cm^{-1}. The dotted line shows the results of absorbance change depending on the molar ratio; (△) 290, (○) 449 nm.

To explain this remarkable difference in the apparent composition of the ion pair formed, the most probable pathway is further reduction of $Mg^{2+}\cdot TCQ^{\cdot -}$ once produced on the electrode surface. Judging from the fact that 1 mol of Mg^{2+} was consumed per mol TCQ in the thin-layer cell, the electron transfer of eqn. (1) is assumed to proceed at the electrode surface after the formation of $Mg^{2+}\cdot TCQ^{\cdot -}$.

$$Mg^{2+}\cdot TCQ^{\cdot -} + e^- \longrightarrow Mg^{2+}\cdot TCQ^{2-} \qquad (1)$$

The intermediate ion pair, $Mg^{2+}\cdot TCQ^{\cdot -}$, appears able to accept a negative charge and reach electrical neutrality, and is in accord with the previous result that $Mg^{2+}\cdot TCQ^{\cdot -}$ was not detected in the absorption measurement.[1]

This hypothesis is in good agreement with the electrochemical measurements in Fig. 1. That is, the appearance of the P_3 can be attributed to the reduction of $Mg^{2+}\cdot TCQ^{\cdot -}$. Since the reduction potential of $Mg^{2+}\cdot TCQ^{\cdot -}$ was positive relative to TCQ, the electron transfer of eqn. (1) is favourable thermodynamically so as to proceed readily after formation of $TCQ^{\cdot -}$.

Although only the decrease of free $TCQ^{\cdot -}$ has been discussed, whether the product in eqn. (1), $Mg^{2+}\cdot TCQ^{2-}$, has a resonance enhancement effect or not is of significance. This is easily checked by a pulse electrolysis stopped-flow method. Since free TCQ^{2-} can be prepared by a column-electrolysis method similarly to the dianion of DDQ,[4] the absorption spectrum of $Mg^{2+}\cdot TCQ^{2-}$ can be measured by mixing solutions of Mg^{2+} and TCQ^{2-}. From this experiment, its absorption spectrum was found to have no maximum around 488 nm similar to that of $Mg^{2+}\cdot TCQ^{\cdot -}$. Thus, resonance enhancement cannot be expected for $Mg^{2+}\cdot TCQ^{2-}$. This means that the dependence of TLERR signals simply reflects the decrease of free $TCQ^{\cdot -}$, and consequently clarifies the characteristics on the electrode reaction.

In conclusion, a difference of ion-pair formation on the electrode surface and in homogeneous solution can be observed and clarified by comparing the results of the present TLERR method and the previous pulse-electrolysis stopped-flow method. While the measurement in homogeneous solution clearly showed that the contact ion pair, $Mg^{2+}\cdot TCQ^{\cdot -}{}_2$, was formed in MeCN, $Mg^{2+}\cdot TCQ^{2-}$ was found to be the most probable product on the electrode surface. The use of the RR spectroscopy in conjunction with electrochemistry was found to be effective in obtaining mechanistic information. The present approach would be useful in analysing complex electrochemical responses by demonstrating the difference between the electrode surface and the bulk solution.

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