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CAN ADSORPTION BE STUDIED IN THE ELECTRODE POTENTIAL RANGE OF SEVERE HYDROGEN EVOLUTION

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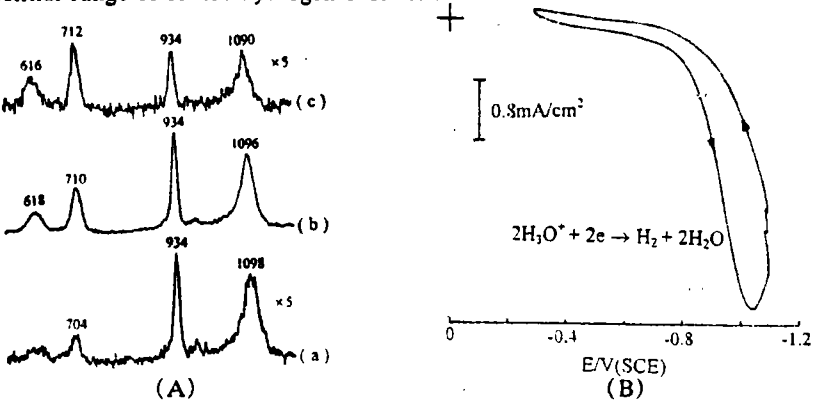
ABSTRACT Surface enhanced Raman spectroscopy (SERS) has been applied to obtain structural information of surface species adsorbed at electrode surface in the electrode potential range of severe hydrogen evolution, which is very difficult to be gained by using most of spectroelectrochemical and conventional electrochemical methods.

It is extremely difficult to study adsorption in electrode potential range of severe hydrogen evolution, e.g., in the electrode potential region negative of −1.2V(SCE) in acidic aqueous solutions or − 1.6V in neutral aqueous solutions, either by conventional electrochemical methods or by spectroelectrochemical techniques. In the differential capacitance, impedance and chronoamperometric studies, the information about adsorption are submerged inevitably in a huge Faradaic current of hydrogen evolution. The vast hydrogen bubbles generated at the surface can change the composition of the electrolyte near the surface and alter the light intensity irregularly, which in general makes a fatal interference to the spectroelectrochemical measurements or even makes the measurements impossible.

There may be several ways to surmount the above problems, at least to some extend. (i) To use the optical internal reflection spectroscopic methods. This method can only reduce the interference of the hydrogen bubbles to some extend since the penetration depth of the solution over which optical sampling occurs is 500 to 2000 Å. (ii) To press the electrode against the cell window. With the help of such a very thin layer cell configuration the hydrogen gas can only form very fine bubbles so that neither the incident nor the scattering (or reflecting) light intensities would be altered seriously by vigorous hydrogen evolution. However, the ohmic drop in the thin layer should be taken into account. (iii) To utilize the surface enhanced effect. When the surface enhanced factor is 10^5, it means that a monolayer adsorbate can be considered as equal to a million layers under normal condition. The composition of this 'a million layers' and the corresponding signal are not influenced at all by the hydrogen bubbling. The drawback is that the surface enhanced effect has only been found for a few metals.

By taking advantages of (ii) and (iii), i.e., using a thin layer cell configuration and surface enhanced Raman spectroscopy (SERS), we have studied the following three systems in this particular electrode potential region. (a) The adsorption of water molecules at around -1.8V has been investigated in solutions containing ClO_4^- or SO_4^{2-} with various concentrations (0.1—8.0mol/L) and/or various cations. The interesting results obtained reveal that the adsorbed water with highly orderd structure may orient with one hydrogen atom ending to the surface at very negative electrode potentials[1,2]. (b) The coadsorption of thiourea with ClO_4^- at Ag electrode in a wider electrode potential range can be observed in acidic solutions. At around -1.1 V the SERS band at 934 cm^{-1} from the coadsorbed ClO_4^- decreases much sharply than other bands from thiourea (Fig. 1(A)), indicating that the coadsorbed anion is more strongly repelled out by the negative charge of the surface. In contrast, it is impossible to obtain the same information using electrochemical differential capacitance method due to the huge Faradaic current of hydrogen evolution at around -1.1 V (Fig. 1(B)). (c) 2-mercaptopyrimidine (2MP) has been found to be adsorbed at silver electrodes in a wide electrode potential range (-0.3—-1.8 V). It is of special interest that the SERS spectra become dramatically different as the electrode potential is moved to the region of hydrogen evolution. By the systematic SERS study one can assume that hydrooligomerization of 2MP takes place at the electrode potentials of hydrogen evolution[3]

It is necessary to point out that the SERS results are more reliable and easier to interpret because some special surface complexes when the SERS active sites are decomposed or removed in the very negative electrode potential region, and only the electromagnetic enhancement mechanism plays a key role. It has been demonstrated that some important information can be extracted to describe the structure of the double layer and understand its effect on the mechanisms of electrode reactions in the electrode potential range of severe hydrogen evolution.



(A) (B)

Fig. 1(A) SERS spectra of silver electrode at various electrode potentials: (a) -0.3 V, (b) -0.7 V and (c) -1.1 V (SCE). (B) Cyclic voltammogram of silver electrode with a sweep rate of 50mV/s. Solution is 1mol/L Thiourea + 0.01mol/L $HClO_4$ + 0.1mol/L $NaClO_4$.

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