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In Situ Raman Spectroelectrochemical Characterization of the Prussian Blue/ Platinum Modified Electrode

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Detailed abstract: Prussian Blue is known to be deposited electrochemically on the electrode surface, producing a dense redox active layer. Since the Prussian Blue modified electrode was first reported by Neff in 1978[1], different in situ spectroelectrochemical techniques have been widely used to investigate its electrochemical mechanism[2~4]. But no research work related to the in situ Raman spectroscopic studies on it has been reported. In this paper we try to characterize the nature of thin Prussian Blue films on platinum substrates with in situ Raman spectroelectrochemical technique.

A Super LABRAM confocal microscopic Raman spectrometer (Dilor) with a He-Ne laser (632.8 nm) and CHI604A electrochemical Analyzer (USA) were used here. Cyclic voltammetry was used to prepare Prussian Blue film modified platinum electrode. The platinum electrode potential was cycled at a scan rate of 50 mV/s between 0 and 0.5 V (vs. SCE).

As shown in figure1, the in situ Raman spectra obtained here characterized two cycles of voltammetric process of the Prussian Blue modified platinum electrode in a potassium chloride solution (1 mol/L) between 0.5 V and - 0.1 V (vs. SCE) with a scan rate 1 mV/s. The observed spectra demonstrated the change of intensities and shifts of those characteristic Raman frequencies related to the coordination structures of Prussian Blue and its reduced form, Prussian White.

From these spectra, intensity changes of those related characteristic Raman lines characterized the stability and reversibility of the Prussian Blue film obviously. As shown in Fig. 2(a), at the beginning of the process, the characteristic Raman frequencies of Prussian Blue remarkably

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appeared at 2 089 cm^{-1}, 2 123 cm^{-1} and 2 154 cm^{-1}. When the scanning potential arrived at the range 0.20～0.15 V, which is somewhat lower than the reduction potential of Prussian Blue film modified platinum electrode, three peaks can be observed at 2 058 cm^{-1}, 2 109 cm^{-1} and 2 140 cm^{-1} respectively [Fig. 2 (b)]. Finally, as shown in Fig. 2(c), at the potential range of -0.10～-0.05 V, characteristic peaks are located at about 2 048 cm^{-1}, 2 095 cm^{-1} and 2 130 cm^{-1}. At this moment, intensities of these peaks decreased to their minimum. These Raman frequencies should be related to the reduced state of Prussian Blue, i.e. Prussian White. Subsequently, with the potential scanning inversely, the intensities and shifts of these characteristic Raman lines changed reversibly.

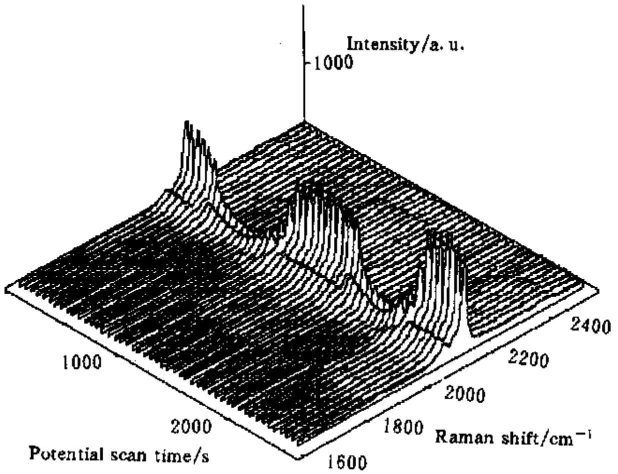

Fig. 1 Three dimensional electrochemical in situ Raman spectra of Prussian Blue modified platinum electrode in 1 mol/L KCl solution (pH 4)

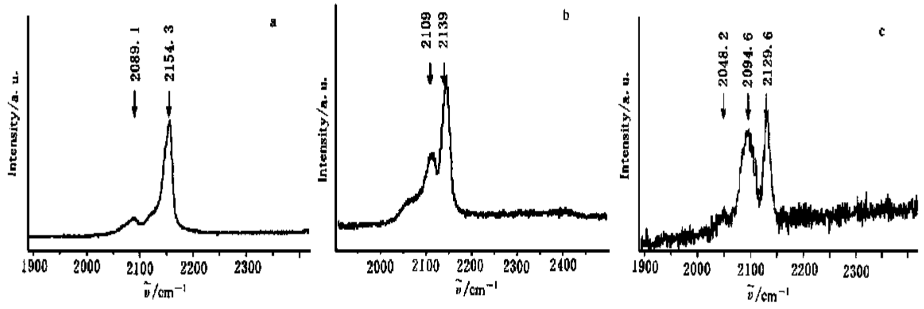

Fig. 2 In situ Raman spectra of Prussian Blue modified platinum electrode in a cyclic voltammetric process. The potential range: -0.10～0.50 V (vs. SCE), scan rate: 1 mV/s. (a) 0.50～0.46 V, (b) 0.20～0.15 V, (c) -0.10～-0.05 V.

As a matter of fact, the basic structure of Prussian Blue is a three-dimensional polymeric network consisting of alternating ferric and ferrous ions on cubic lattice sites. The ferric ion is coordinated to the nitrogen atoms, and the ferrous ion to the carbon atoms, of the bridging cyanide ligands. In the presence of potassium ion, a thin film of Prussian Blue [$KFeFe(CN)_6$], which is

modified on a platinum substrate, can be reduced to Prussian White [$K_2FeFe(CN)_6$] at 0.195 V (vs. SCE). The structural difference between Prussian Blue and Prussian White lies in that bridging cyanide ligands are coordinated to iron ions in different valence states. Therefore, it was inferred that the peaks located at 2 089 cm^{-1}, 2 123 cm^{-1} and 2 154 cm^{-1} should be assigned to the characteristic Raman vibrational frequencies of the bridging cyanide ligands in the structure Fe(II) - C ≡N - Fe(III) in Prussian Blue, and the peaks located at 2 048 cm^{-1}, 2 095 cm^{-1} and 2 130 cm^{-1} to those in the structure Fe(II) - C ≡N - Fe(II) in Prussian White.

Key words: Prussian blue, Modified electrode, Raman spectroelectrochemistry

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普鲁士蓝膜修饰铂电极的现场拉曼光谱电化学表征

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摘要:　采用现场拉曼光谱电化学技术表征了普鲁士蓝膜修饰铂电极的循环伏安过程. 结果显示,随着修饰膜的微观结构由普鲁士蓝向普鲁士白或相反过程转化,表征两种不同结构的拉曼特征振动谱峰及其强度变化呈现出明显的可逆特征.

关键词:　普鲁士蓝;修饰电极;拉曼光谱电化学