fraction at the critical charge transfer is 0.32 ± 0.03 ,¹⁴ compared to the calculated value of 0.29. It is also less than the maximum possible place-exchange fraction of 0.33.

To summarize the course of reaction steps just discussed, the following model of surface oxidation can be deduced by assuming an ideal ($\sqrt{3} \times \sqrt{3}$)*R*30° structure upon completion of a monolayer oxidation. Note that the coefficients in the equations are not simple stoichiometric ratios of the chemical reactions but indicate the fractional coverage by the platinum species.

$$Pt + \frac{1}{3}H_{2}O \rightarrow \frac{2}{3}Pt + \frac{1}{3}PtOH + \frac{1}{3}H^{+} + \frac{1}{3}e^{-} \quad (1) \frac{2}{3}Pt + \frac{1}{3}PtOH + \frac{2}{3}H_{2}O \rightarrow \frac{2}{3}PtOH + \frac{1}{3}OPt + H^{+} + e^{-} \quad (2) \frac{2}{3}PtOH + \frac{1}{3}OPt \rightarrow \frac{2}{3}PtO + \frac{1}{3}OPt + \frac{2}{3}H^{+} + \frac{2}{3}e^{-} \quad (3)$$

Note that OPt represents a place-exchanged PtO. The first and second steps occurred abruptly corresponding to Peaks I and II in the voltammogram, respectively, while the last step occurs continuously over a wide potential range corresponding to the slow and continuous rise of the anodic current.

Conclusions

In this article we have reviewed elementary aspects of the synchrotron-based x-ray-scattering technique for the investigation of the structure of electrochemical interfaces and some of its preliminary applications for the investigation of "buried" liquid/solid interfaces. We have shown its capability for providing detailed structural information on liquid/ solid interfaces. We expect that, as the operation of the high-energy synchrotron sources advances, liquid/solid interface studies will also advance closer to the maturity level of current UHV surface science and beyond.

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