In situ and non situ surface x-ray scattering studies of in plane Cs\textsuperscript{+} ordering in Helmholtz planes of Pt(111) surface

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Abstract

In-plane ordering of Cs\textsuperscript{+} layers in Helmholtz planes was studied on Pt(111) surface in 0.1 M CsF electrolyte solutions with synchrotron surface x-ray scattering techniques. The ordering was measured in a new transmission cell, designed for in situ and non situ measurements and high-temperature sample annealing all in the cell without sample transfer steps. At −850 mV vs. Ag/AgCl, (2×2) in-plane scattering peaks were weak under in situ condition and grew rapidly under non situ condition as the surface emersed from the electrolyte. The models for the (2×2) structures are presented and differences between in situ and non situ conditions are discussed.
1. Introduction

The structure and motion of ions in electrochemical double layers (EDL) is key information in basic electrochemistry and electrocatalysis (Markovic 2013). EDL is traditionally described as diffuse distributions of cations and anions, proposed by Gouy and Chapman (Bard and Faulkner 2001) and further developed extensively over decades (Gurney 1935, Grahame 1947, Wagner and Ross 1983, Grassi, Daghetti et al. 1987, Trasatti 1987, Ardizzone, Fregonara et al. 1990, Daghetti, Romeo et al. 1993, Trasatti and Doubova 1995). The early development of the diffuse EDL models can be found in an extensive review (Parsons 1990). In recent years, synchrotron x-ray techniques have been extensively used for studies of chemical and electrochemical double layers: on the membrane-aqueous interfaces using x-ray standing wave technique (Bedzyk, Bommarito et al. 1990), on the solid/liquid interfaces using crystal truncation rod measurements (Lucas, Thompson et al. 2011), and on liquid/liquid interfaces using x-ray reflectivity techniques (Luo, Malkova et al. 2006).

The EDL in previous studies was considered for the distribution of ions only along the direction of surface normal. The assumption is that the ions have no in-plane ordering and distributed randomly parallel to the surface. However, for potentials significantly away from the potential of zero charge (PZC), the charged ions, sometimes hydrated, can be strongly pulled toward the solid surface and form relatively dense layers of the ions. The dense layer of the ions with repulsive interactions due to the same charges may induce significant in-plane structures that have not been observed heretofore. This in-plane structure, the focus of this study, differs from those occurring in chemisorption accompanying faradaic charge transfer reactions. In the case of Cs⁺ studied here, the cation does not specifically chemisorb even at the largest negative potential that we measured in situ. Yet, in-plane ordering peaks are identified under in situ as well as non
situ (Stuve, Krasnopoler et al. 1995) conditions using the emersion technique (Kolb, Rath et al. 1983, Kolb 1987, Zurawski, Rice et al. 1987).

2. Experimental

2.1 Cell Design

A new transmission cell was designed and built for this experiment. In this cell, the sample surface can be annealed by an induction heater and immersed to an electrolyte without exposing the surface to ambient conditions. In this way, the pristine surface prepared is immediately used for electrochemical/x-ray measurements. The cell geometries are schematically shown in Figure 1. In (a), x-rays diffract from the surface through the electrolyte typically 2~3 mm thick. The x-ray transmission tends to produce large background scattering. The background scattering can be subtracted but the signal to noise ratio limits the detection of weak peaks. In (b), x-rays do not go through the water, therefore, the background scattering is much lower. The electrochemical control is lost and the situation is equivalent to the non situ condition in the UHV transfer experiments (Stuve, Krasnopoler et al. 1995). In (c), the inner quartz tube, filled with electrolyte
and assembled with reference and counter electrodes, is retracted. Then, the Pt(111) crystal with the long Pt wire tail was raised to the height of the coil of the pre-aligned induction heater. This configuration is used for sample annealing.

2.2 Synchrotron X-ray Measurements

Synchrotron x-ray measurements were performed at 11ID-D beamline equipped with a ‘4S+2D’ geometry six-circle diffractometer (You 1999) at Advanced Photon Source (APS). Pt(111) surface, precut and polished, had a miscut of <0.1°. The hexagonal (hex) index \( a^* = 4\pi\sqrt{2} / \sqrt{3}a \) and \( c^* = 2\pi / \sqrt{3}a \) where \( a=3.9242\AA \) of face-centered cubic (fcc) structure was used in the experiments (Huang, Gibbs et al. 1990) where \( (111)_{\text{fcc}}, (\overline{1}1\overline{1})_{\text{fcc}}, \) and \( (200)_{\text{fcc}} \) are indexed to \( (003)_{\text{hex}}, (101)_{\text{hex}}, \) and \( (012)_{\text{hex}} \), respectively. 0.1 M CsF and CsCl electrolyte was prepared from the CsF and CsCl solid salt of 99.99% in metals-basis purity from Puratronic® dissolved in 18 MΩ·cm water. The results in CsCl are not reported here because the results were essentially identical to those in CsF. The potential range used in the study was −850 mV to 400 mV vs. Ag/AgCl reference electrode. The counter electrode was a platinum wire. −850 mV was used for in situ Cs⁺ structure measurements and also as the emersion potential for non situ measurements. The platinum crystal was annealed to ~1500 K before each set of experiments in dry Ar-3%H₂ inert gas flow. The Pt(111) crystal is cooled to room temperature and the gas flow is switched to bubbled humid N₂. The surface was checked for readiness and pre-oriented by x-ray reflectivity and Bragg diffraction before made in contact with the electrolyte droplet. In this way, the exposure of x-rays to the electrolyte was minimized. During the measurements, the x-ray shutter was open only for signal counting to minimize the x-ray exposure to the electrolyte. The open circuit potential can drift during x-ray exposure (Nagy and You 1995). Therefore,
precautions were exercised and experiments were repeated with different intensities of incoming x-rays to ensure that the results presented here is in any way affected by the x-ray exposure.

### 3. Results and Discussion

*In situ* experiment was performed first. While the potential was held at $-850$ mV, various in-plane vector positions were scanned until a weak surface peak at $(0.5 \ 0.5 \ 0.33)$ was identified. Then, the electrolyte droplet was withdrawn from the surface (Figure 1b) at $-850$ mV while holding the surface vertical for a quick emersion. The scan through $(0.5 \ 0.5 \ 0.33)$ was immediately repeated and several successive scans are shown in Figure 2. The integrated intensities measured *in situ*, at 1 min, at 6 min, and at 64 min after the emersion were $0.9(1)$, $2.2(1)$, $8.9(1)$, and $8.5(1)$, respectively. The scan at open circuit was flat within the noise, not shown here for clarity. The intensity grows rapidly for the first 6 min after the emersion. It is important to note that the peak intensity goes back to the *in situ* condition if the surface is re-immersed immediately after the 1 min measurements. This indicates that the Cs$^+$ remains
hydrated up to this point and the intensity increases mainly due to the lower background. If the surface is re-immersed after several min, however, the intensity remains strong and unresponsive to the applied potential, indicating that Cs\(^+\) is dehydrated, at least partially, and possibly chemisorbed (or strongly adsorbed) to Pt(111) surface. In this case, the surface has to be reannealed to recover a clean surface. The intensity decreases eventually even under the humid N\(_2\) flow in an hour after the emersion. The surface is no longer clean, probably due to the oxygen impurities in the cell. At this point, again, the surface has to be re-prepared to recover the pristine surface condition.

The superlattice peak at (0.5 0.5 0.33) indicates a (2\(\times\)2) structure. In order to determine the structure, three (2\(\times\)2) peaks, (1 -0.5 0.33), (0.5 0 0.33), and (0.5 0.5 0.33), were measured. Pt(0 1 0.5) was also measured as a calibration point. These peaks are compared in Figure 3. The inset
shows the reciprocal space map with the curved green arrows indicating the directions of the $\phi$ scans. Comparing the widths, the superlattice peaks are $\sim$20 times broader than the Pt peak. The longitudinal scans (not shown) are also more than $\sim$10 times broader. These scans indicate that the average domain size of the superlattice is in the order of a few tens nm. The intensities of these peaks all show little dependence on $L$ values, indicating that they are indeed from a monolayer structure. Pt(0 1 0.5), is the anti-Bragg peak between two Bragg peaks, (0 1 2) and (0 1 −1). The intensity of this peak can be estimated from an expression, $\left| \frac{f_{Pt}}{1-e^{i2\pi(0L-1)/L}} \right|^2$, for (0 1 L) crystal truncation rod(Robinson 1986), where $f_{Pt}$ is the form factor for a platinum atom. The form factors for the diffraction angles concerned here are essentially the atomic numbers ($f_{Pt} = 78$). The calculated intensity of (0 1 0.5) is then $[4(78/2)]^2$ for a (2×2) unit cell where 4 comes from 4 atoms in a unit cell.

In calculating the (2×2) superlattice peaks, three models shown in Figure 4 are considered. There are other possibilities. However, most of them can be considered as the variations or combinations of the three models by moving the Cs$^+$ positions to non-symmetric sites.
Therefore, only these three models will be considered: two sublattice model (a), three sublattice model (b), and a single sublattice model (c). Since Cs\(^+\) ions are hydrated, water molecules are incorporated into the lattice. However, they are not included in the calculations because they are weak scatters. The calculated intensities for the three models and the experimental intensities are shown in Table 1. The all values are scaled by setting the intensity of (0 1 0.5) as unity.

The experimental intensities in Table 1 are from the non situ peaks shown in Figure 3. The intensities for (0.5 0.5 0.33) and (1 −0.5 0.33) are 10\% and 9\%, respectively, and that for (0.5 0 0.33) is 3\%. The Debye-Waller (DW) factors of Cs\(^+\), which are unknown, are not included. Therefore, the calculated intensities are the upper bounds and the the experimental intensities cannot be similar, if the Cs\(^+\) layer is as well ordered as Pt layer, or larger than the calculated ones. This eliminates the single sublattice model (c). Among (a) and (b), (b) can easily eliminated because the measured intensity of (0.5 0 0.33) is small but not zero. In the case of model (a), the intensities make sense if the DW factor significantly reduced the intensity. The Cs\(^+\) ions are expected to be quite disordered with significant domain boundaries because Cs\(^+\) domain sizes are much smaller than the Pt(111) surface domain size as discussed in Figure 3. The DW factor is \( e^{-\left(\frac{\sigma q^2}{3}\right)} \), where \( q = 4\pi \sin(\theta)/\lambda \) and \( \sigma \) is the mean squareed displacement. The 80\% reduction of the DW factor suggests \( \sigma = 0.9 \) Å, which is \( \sim 33 \% \) of the Pt-Pt distance. The measured intensity ratio between (0.5 0.5 0.33) and (0.5 0 0.33) also agrees with the calculated ratio.

Table 1. The comparison of the calculated (2×2) intensities to the measured non situ and in situ intensities for the models shown in Figure 4. The in situ intensities are measured in 1 min after emersion. All intensities are normalized by (0 1 0.5) intensity.

|       | (a) | (b) | (c) | Non situ intensity | In situ intensity |
|-------|-----|-----|-----|--------------------|------------------|
| (0.5 0.5 0.33) | 0.50 | 1.12 | 0.09 | 0.10(1)            | 0.03(1)          |
| (1. −0.5 0.33) | 0.50 | 1.12 | 0.09 | 0.9(1)             | 0.03(1)          |
| (0.5 0.0 0.33) | 0.12 | 0    | 0.09 | 0.03(1)            | 0.03(1)          |
For the *in situ* condition, the (0.5 0.5 0.33) intensity (Figure 2) is barely above the background. The *in situ* intensity of (0.5 0 0.33) is also close to the background (not shown). In the first scan immediately after emersion, the (0.5 0.5 0.33) intensity is ~3% of the (0 1 0.5) intensity or ~25% of the full *non situ* intensity. The delay time for the first scan is about a minute, which includes the time for withdrawing the electrolyte, interlocking the door of the x-ray hutch, and scanning the peak. Likewise, the (0.5 0 0.33) intensity, measured immediately following the first (0.5 0.5 0.33) measurement (in ~2 min after the emersion), is again ~3% of the (0 1 0.5) intensity. Note that the *non situ* (0.5 0 0.33) intensity does not change over time while the *non situ* (0.5 0.5 0.33) and (1 −0.5 0.33) peaks grow in time (Figure 2). The integrated intensities measured within 2 min indicate that the structures are different between the *non situ* and *in situ* conditions. It suggests that additional Cs⁺ ions must be incorporated into the (2×2) structure during the first several minutes after emersion, probably from the thin electrolyte layer invisible yet still remaining after the emersion. Therefore, the *in situ* (2×2) structure should be close to the model (c) where the intensities of (0.5 0.5 0.33), (1 −0.5 0.33), and (0.5 0 0.33) are all weak and similar each other. Since the calculated intensities of the model (c) are 9% each for (0.5 0.5 0.33), the ~3% is reasonable for the model (c). This is also consistent with our recent crystal truncation rod measurements of the same system [Kawaguchi, 2017 #869] [Liu, 2017 #1029] where the direct inversion technique was used to obtain the Cs⁺ peak density of ~0.7 e⁻/Å³ at 3.5 Å distance above the Pt(111) surface. Under this scenario, the highly disordered hydrated Cs⁺ ions maintain the short-range single-sublattice (2×2) model (c) structure in electrolyte. As the solution thins in several min after emersion, however, additional Cs⁺ ions are incorporated into the lattice to form the two-sublattice model (a) structure.
4. Conclusions

In situ and non situ studies of Cs⁺ cations in Helmholtz planes were performed on Pt(111) surface in 0.1 M CsF electrolyte using synchrotron in-plane x-ray diffraction. In both conditions, (2×2) peaks were observed. The in situ (0.5 0.5) peak intensity was weak and consistent with the simple (2×2) structure with a single sublattice occupied by Cs⁺. The non situ (0.5 0.5) peak was strong, consistent with the model where two Cs⁺ sublattices are occupied. These observations lead to two important conclusions. First, the hydrated cations can order in the first Helmholtz plane under the large polarization. This is true at least for hydrated Cs⁺ layer in the Helmholtz planes. The hydrated ions are likely not registered to the Pt(111) substrate while the chemisorbed ions are registered. Second, the structures in non situ condition can be different from those in in situ condition. The non situ structures provide still useful information about the electrochemical surface. However, the hydration of the cations may change and the surface density of the cations can increase because of dehydration during and after the emersion process.

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