

Reduction of the ruthenium dioxide (100) surface: origin of ultracapacitance

T.E. Lister, Y. Chu, H. You, and Z. Nagy

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439 USA

Introduction

Ruthenium dioxide is the most investigated and well-known candidate oxide material for ultracapacitors, and it exhibits the most ideal ultracapacitor behavior. Additionally, its pseudocapacitance was generally found to dominate over the simple double-layer capacitance. The essential surface reaction of the RuO_2 electrode is expected to cover the full range of Ru^{2+} , Ru^{3+} , and Ru^{4+} oxidation states. We studied the transition from Ru^{3+} to Ru^{4+} and the reverse transition.

Methods and Materials

Single crystals of RuO_2 are grown in a multizone furnace using a vapor transport method under oxygen flow. A selected crystal embedded in a Teflon perk was mounted in an *in situ* electrochem/x-ray cell. The experiment was performed in 0.5 M sulfuric acid.

Results

The ruthenium dioxide forms a rutile structure exhibiting a tetragonal symmetry ($a_0 = b_0 = 4.50$, $c_0 = 3.11$ Å). CV measurements in 0.5 M sulfuric acid exhibit a sharp peak of charge transfer at a potential approaching the hydrogen evolution potential at ~ 0 V vs. Ag/AgCl 3 M NaCl reference (this potential scale is used throughout this report) as shown in Figure 1A. The total amount of charge transfer is approximately 0.5 electron per ruthenium atom and the sharpness clearly indicates that this feature is a surface reaction phenomenon. At the corresponding potentials, the x-ray intensity measured at surface-sensitive orientations [for example, at (1.6 0 0) as shown in Figure 1B)] clearly indicates that the reaction is accompanied by a surface structural change.

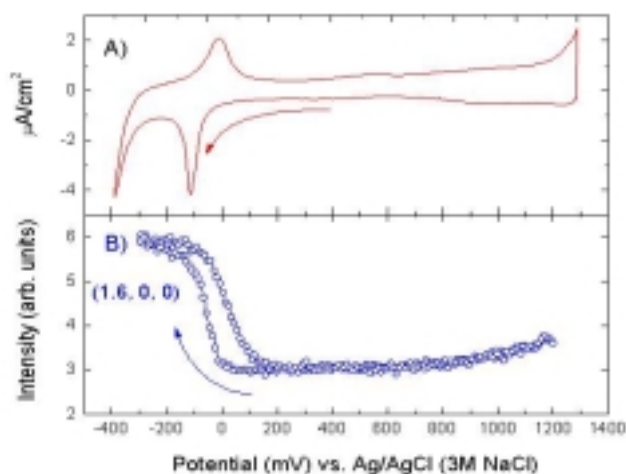


Figure 1: (A) CV of $\text{RuO}_2(100)$ surface reaction. (B) X-ray intensity as a function of potential. The scan direction is indicated by the arrows.

Discussion

Our analysis of the full x-ray reflectivity data [four rods (00L), (10L), (01L), and (11L) were measured and analyzed] indicates that one oxygen layer termination is maintained despite a significant expansion of the top ruthenium layer and repositioning of the oxygen atoms during reduction and oxidation processes. At the oxidizing potential above ~ 0 V, the layer spacing of the top ruthenium layer is closely maintained to that of the bulk, while the positions of the top oxygen atoms are significantly changed from their bulk positions. The oxygen-ruthenium bond stretches for the oxygen atom to sit on the tetrahedral site above, in an equal distance from the four ruthenium atoms as shown in Figure 2. In this way, the top ruthenium atoms are well protected from further oxidation while maintaining the symmetry and charge neutrality for Ru^{4+} . At reducing potential below ~ 0 V, however, the oxygen atoms retract back to the bulk positions while the top ruthenium plane is approximately 5% expanded. In this condition, the top ruthenium atoms and their bonds to oxygen atoms below are elongated. The elongated bonds are consistent with the change in the oxidation state to Ru^{3+} whose bonding to oxygen is expected to be weaker than that of Ru^{4+} . Furthermore, there is ample space above the ruthenium atoms where the second-layer oxygen atoms would be in the bulk structure. This space opened up because the oxygen atoms retracted to the bulk positions. The opening is large enough for a water molecule to fit comfortably!

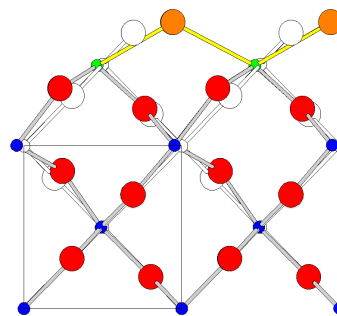


Figure 2: The structure of (100) surface at OCP. The open circles indicate the bulk positions.

From our x-ray studies, we can conclude that the observed reaction has to include the adsorption of a species invisible to x-rays at the cathodic peak in the CV shown in Figure 1A and desorption at the anodic peak. Since H^+ exists as hydronium ions in solution, our observations point to the adsorption and desorption of hydronium ions to and from the top oxygen atoms. The bonding of a hydronium ion must occur to an oxygen atom and is expected to be floppy, leading to a very large motion of the hydronium. In fact, such a scenario is consistent with our data. If the motion of hydronium ions is indeed large, they may be unobservable with

off-specular reflectivity but can remain observable in the specular reflectivity scans. Indeed, there is a region of scattering that is unexplained by the structural models described above. The extra scattering density seen in the specular reflectivity scan is consistent with the scenario of “floppy hydronium” adsorption onto the open cages on the surface, most likely bonded to the top-most oxygen.

Acknowledgments

The experiment was performed at beamlines 12-ID-B and 12-BM-B at the Advanced Photon Source (APS). The use of APS was supported by the U.S. Department of Energy (DOE), Basic Energy Sciences (BES), Office of Science, under Contract No. W-31-109-Eng-38. This work was supported by Chemical Science Program of DOE, BES.