

Corrosion Protection of Metal Surface by Cationic Species

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Summary

The cationic species in the outer Helmholtz plane (OHP) formed at a metal / electrolyte interface affects electrochemical processes remarkably, but the structure and the potential dependence have been controversial for decades. We have successfully determined the detailed OHP structure composed of Cs^+ above $c(2 \times 2)$ -Br on Ag(100) electrode using in-situ surface X-ray diffraction in electrochemical environments. Hydrated Cs^+ cation is accommodated in the hollow site of $c(2 \times 2)$ -Br layer. The coverage of Cs^+ (q_{Cs}) in the OHP and the distance from the adsorbed Br layer $d_{\text{Cs-Br}}$ are optimized at various potentials. The value of q_{Cs} decreases with the increase of $d_{\text{Cs-Br}}$ at positive potentials, because the repulsive electrostatic forces increase. The dielectric constant in the double layer, which is estimated from structural parameters, is comparable to that of well-orientated ice phase. We also revealed the promotive effect of alkali metal cations on Br adlayer formation on an Ag(100) electrode by in-situ measurement of the X-ray specular rod. Alkali metal cations in the electrical double layer affect the onset potential of Br adsorption and the order-disorder transition. We determined the Cs structure in the electrical double layer during Br adlayer formation, and found that (1) the Cs structure depends on the coverage of adsorbed Br and (2) the amount of Cs increases at the initial stage of Br adlayer formation. Structural analysis suggests that hydrated Cs is localized in the area around adsorbed Br via non-covalent interactions. Formation of a Cs-Br complex promotes Br adsorption.