In Situ Observation of Mass Change of Active Material for Positive Electrode in Lead-acid Battery using Electrochemical QCM Technique - M. Taguchi (Akita University)

In order to investigate the early stages of discharge-charge of the active materials for positive electrode in the lead-acid battery, a PbO₂ thin film was prepared by reactive sputtering, and then cyclic voltammetry on the PbO₂ film electrode was repeated 5 times in various H₂SO₄ solutions ranging from 0.1 to 2.0 kmol m⁻³ in concentration at 303 K. The mass change of the PbO₂ film electrode was in situ observed using the electrochemical quartz crystal microbalance (EQCM) technique. The mass of the active material of positive electrode, PbO₂ increases during the discharge reaction of PbO₂ → PbSO₄ and it decreases during charge reaction of PbSO₄ → PbO₂. A part of the discharge product, PbSO₄ was not restored to its original state, PbO₂ on 1 ~ 3 cycles of discharge-charge, although the mass change curves had the loop shapes on 4 ~ 5 cycles. The discharge-charge became steady-state and the current efficiency of discharge was nearly equal to that of charge on and after 4 cycle. On the other hand, the average grain size of the discharge product, PbSO₄ in 0.1 kmol m⁻³ H₂SO₄ solution was about 0.35 μm and it was considerably smaller than those in 0.5 ~ 2.0 kmol m⁻³ H₂SO₄ solutions. Moreover, the utilization efficiency of PbO₂ in the former solution is approximately 6 ~ 8 % higher than those in the latter solutions. It may be concluded from the results that the utilization efficiency of PbO₂ depends on the shape of the PbSO₄ crystal produced by the first discharge. Therefore, it seems that refining the grain size of the first discharge product is of great significance for the improvement of the discharge-charge property of the active materials for positive electrode in the lead-acid battery.