In Situ Observation of Mass Change of Active Material for Positive Electrode in Lead-acid Buttery 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 PbO_2 thin film was prepared by reactive sputtering, and then cyclic voltammetry on the PbO_2 film electrode was repeated 5 times in various H_2SO_4 solutions ranging from 0.1 to 2.0 kmol m^{-3} in concentration at 303 K. The mass change of the PbO_2 film electrode was in situ observed using the electrochemical quartz crystal microbalance (EQCM) technique. The mass of the active material of positive electrode, PbO_2 increases during the discharge reaction of $PbO_2 \rightarrow PbSO_4$ and it decreases during charge reaction of $PbSO_4 \rightarrow PbO_2$. A part of the discharge product, $PbSO_4$ was not restored to it original state, PbO_2 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, $PbSO_4$ in 0.1 kmol m^{-3} H_2SO_4 solution was about 0.35 μm and it was considerably smaller than those in 0.5 ～ 2.0 kmol m^{-3} H_2SO_4 solutions. Moreover, the utilization efficiency of PbO_2 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 PbO_2 depends on the shape of the $PbSO_4$ 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.