

Silver nanowires and nanodendrites synthesized by plasma discharge in solution for the catalytic oxygen reduction in alkaline media

김희근^{a,*}, 송면규^a, 김동우^a, 이상을^a

^a한국항공대학교 항공재료공학과(E-mail:ndkim2@naver.com)

초 록: Pt is still considered as one of the most active electrocatalysts for ORR in alkaline fuel cells. However, the high cost and scarcity of Pt hamper the widespread commercialization of fuel cells. As a strong candidate for the replacement of Pt catalyst, silver (Ag) has been extensively studied due to its high activity, abundance, and low cost. Ag is more stable than Pt in the pH range of 8~14 as the equilibrium potential of Ag/Ag⁺ being ≈ 200 mV higher than that of Pt/PtO. However, Ag is the overall catalytic activity of Ag for oxygen reduction reaction(ORR) is still not comparable to Pt catalyst since the surface Ag atoms are approximately 10 times less active than Pt atoms. Therefore, further enhancement in the ORR activity of Ag catalysts is necessary to be competitive with current cutting-edge Pt-based catalysts. We demonstrate the architectural design of Ag catalysts, synthesized using plasma discharge in liquid phase, for enhanced ORR kinetics in alkaline media. An attractive feature of this work is that the plasma status controlled via electric-field could form the Ag nanowires or dendrites without any chemical agents.

The plasma reactor was made of a Teflon vessel with an inner diameter of 80 mm and a height of 80 mm, where a pair of tungsten(W) electrodes with a diameter of 2 mm was placed horizontally. The stock solutions were made by dissolving the 5-mM AgNO₃ in DI water. For the synthesis of Agnanowires, the electricfield of 3.6kVcm⁻¹ in a 200-ml AgNO₃ aqueous solution was applied across the electrodes using a bipolar pulsed power supply(Kurita, Seisakusyo Co. Ltd). The repetition rate and pulse width were fixed at 30kHz and 2.0 us, respectively. The plasma discharge was carried out for a fixed reaction time of 60 min. In case of Ag nanodendrites, the electric field of 32kVcm⁻¹ in a 200-ml AgNO₃ aqueous solution was applied and other conditions were identical to the plasma discharge in water in terms of electrode configuration, repetition rate and discharge time. Using SEM and STEM, morphology of Ag nanowires and dendrites were investigated. With 3.6 kV/cm, Ag nanowire was obtained, while Ag dendrite was constructed with 32 kV/cm. The average diameter and length of Ag nanowires were 50 nm and 3.5 um, and those values of Ag dendrites were 40 nm and 3.0 um. As a results of XPS analysis, the surface defects in the Ag nanowires facilitated O₂ incorporation into the surface region via the interaction between the oxygen and the electron cloud of the adjacent Ag atoms. The catalytic activity of Ag for oxygen reduction reaction(ORR) showed that the catalytic ORR activity of Ag nanowires are much better than Ag nanodendrites, and electron transfer number of Ag nanowires is similar to that of Pt (≈ 4).

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