

Structure evolution and Modification of highly active and durable TiO₂@Pt core-shell electrocatalyst for oxygen reduction reaction

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ABSTRACT

Structure evolution and modification of new nanostructured platinum-based oxygen reduction reaction catalysts are the objectives of this study. In previous work, unsupported core-shell TiO₂@Pt particles were proposed as a model catalyst could generate efficient ORR catalyst. Although TiO₂@Pt particles derived from the photo-deposition method could have a completely covered Pt shell structure, and they achieved reasonable ORR catalytic activity. In this work, it is hoped to modify the way of feeding Pt ionic solution from burette to syringe pump, so that the uniformity of photo-deposited Pt and its layer thickness can be further improved. High-resolution transmission electron microscopy (TEM) and elemental mapping images showed that the complete Pt shell on TiO₂ core was formed, and the thickness of Pt shell was around 2 nm as a result of more precise control over Pt growth. The optimized TiO₂@Pt exhibits mass activity of 0.092 mA/μg_{Pt} and specific activity of 0.064 mA/cm², outperforming the commercial benchmark Pt/C. In addition, the unique structure of TiO₂@Pt also possesses excellent stability during the accelerated durability test (ADT). The sample is able to retain 80% of its original mass activity after 50000 cycles.

It is also interesting and important to study the structural evolution of TiO₂@Pt, especially Pt NPs, after such long cycles. Through Cs-STEM we speculate the sample TiO₂@Pt after ADT still have thin platinum layer on Titanium dioxide. It is speculated that TiO₂@Pt undergoes electrochemical scanning, and the low-coordination platinum atom is preferentially dissolved and then deposited on the side of the high-coordinate platinum atom. It was found that the interaction before and after the stability of TiO₂@Pt is unchanged by XAS.

X-ray absorption spectroscopy show that the white intensity of TiO₂@Pt after ADT for finishing stability test is the same as TiO₂@Pt before ADT, indicating that the electronic effect is not attenuated after the stability test and after the Fourier transform of the EXAFS spectral function of the k³ weighted function, the peak value rises after the stability test at

the position of the 2.6 Å platinum-platinum bond. This part should be the platinum particles agglomerated after the stability test.

Keywords: TiO₂@Pt, core shell, photo-deposition, oxygen reduction reaction