

Preparation of Ta, Nb, Ti, and Zr--based Catalysts
for Cathode of Polymer Electrolyte Fuel Cells
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Polymer electrolyte fuel cells (PEFCs) are one of the promising power devices for FC vehicles and residential cogeneration systems; however, huge consumption of platinum-group metals (PGM) for PEFCs constricts the large scale commercialization of PEFCs. Although Fe and Co compounds are frequently attempted to cathode catalysts as N-coordination structures, they are essentially soluble in the strong acidic media and always has a problem in the durability especially at operating temperature of PEFCs around 350 K. The metal-free carbon materials with N-substitution are also regarded as the candidates of cathode catalysts. Carbon materials are durable even in acidic media; however, the activity for oxygen reduction reaction (ORR) is significantly less than transition-metal and transition-metal compound catalysts. The oxides or nitrides of group IV and V elements such as Ta, Nb, and Ti forms stable passivation layer at the interface even in the strong acid, so that they are promising candidates for cathode catalysts. They can act as transition metal compound catalysts with the effect of d-orbitals of metal cations in the compounds.

Our group has proposed several preparation methods of Ta, Nb, Ti, and Zr-based catalysts for PEFCs. The metal species can be well dispersed on carbon black (CB) particles using the polymerized complexes (PC) method especially with addition of N-ligands such as phenanthroline.^{1,2} Nano-particles of Ta, Nb, Ti, and Zr nitrides has been reported to have obvious activity for ORR, and the methods of nanonitride synthesis on CB³ or carbon nanotubes (CNT)⁴ surfaces using meso-porous C₃N₄ has been developed. In this presentation, our newest preparation method of Ta and related metal oxides catalysts utilizing electrodeposition of non-aqueous deposition baths is firstly demonstrated.⁵ The relation of the adsorption behavior of molecularly-adsorbed oxygen to the ORR activity has been studied using temperature programmed desorption (TPD) for nano-nitride catalysts, and the importance of molecularly-adsorbed oxygen on the cathode catalysts is secondly discussed.⁶

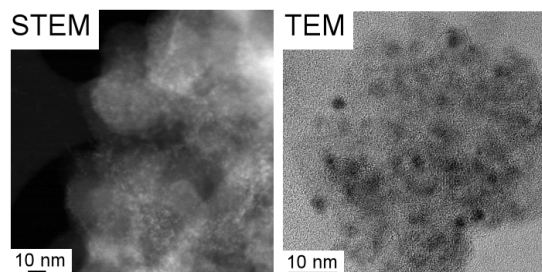


Fig. 1. The images of Ta electrodeposited CB particles by transmission electron microscope (TEM) and scanning TEM (STEM).⁵

Most of Ta, Nb, Ti, and Zr compounds are not soluble in aqueous solutions even acidic and alkaline conditions and this is consistent with the quite high durability of Ta, Nb, Ti, and Zr-based catalysts in strong acidic condition of PEFCs. Thus, there is no way to electrodeposit these species on CB supports from any

aqueous deposition bath. Thus, ethanol solutions of Ta and Nb chlorides with supporting electrolyte of NaClO₄ were used as the deposition baths. A CB-coated carbon paper with small amount of Nafion ionomer was used as the substrate and the electrodeposition was performed at -0.5 V_{Ag/AgCl} for 10 s. Ta(V) and Nb(V) are hard to be reduced to the metallic valency, so that it is supposed that they are reduced to (IV) or (III) and immobilized onto CB surfaces. Fig. 1 shows STEM and TEM images of Ta electrodeposited catalysts on CB. The Ta species, which is oxide or hydroxide, seems to be dispersed with a few nm particle sizes. The electrochemical behavior of Ta electrodeposited CB is shown in Fig. 2. The Ta catalysts shows the onset potential for ORR as high as 0.92 V_{RHE}.

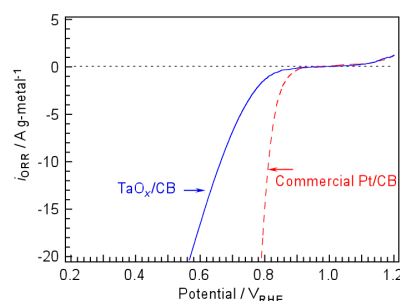


Fig. 2. The comparison of Ta electrodeposited CB and commercial Pt/CB in *I-E* curves in the 0.1 M H₂SO₄ at -5 mV s⁻¹ scan.⁵ The current is difference between O₂ and Ar. The loading amounts of Ta and Pt were 0.016 and 0.025 mg cm⁻².

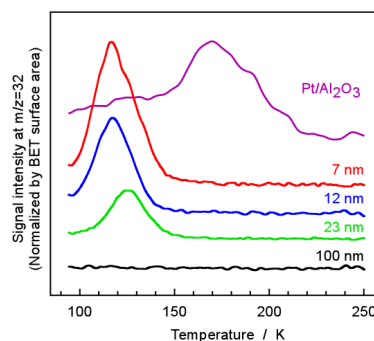


Fig. 3. O₂-TPD spectra of molecularly-adsorbed O₂ from Pt and nano-TiN cathode catalysts with different sizes.

The molecular adsorption of O₂ on the catalyst surface is the primitive step of ORR. TPD spectra of molecularly-adsorbed O₂ from TiN nanoparticles are shown in Fig. 3. The amount and temperature of desorption will be discussed with the performance of cathode catalysts.

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