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Keio University

Thesis Abstract

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Thesis Title

Preparation of Platinum Nanoparticles by Electrochemical Reduction of Bis(acetylacetonato)platinum(II) in Amide-Type Ionic Liquids

Thesis Summary

Platinum (Pt) and Pt nanoparticles are of great interest due to their high catalytic activity in a number of chemical and electrochemical reactions. In recent years, aprotic ionic liquids have gained much attention as an attractive alternative media for electrodeposition of various metals and metal nanoparticles owing to their several excellent physicochemical and electrochemical properties. Bis(acetylacetonato)platinum(II) ($Pt(acac)_2$) is a well known precursor for preparation of Pt nanoparticle. However, electrochemical reduction of $Pt(acac)_2$ has not been studied in depth in ionic liquids yet. In the present study, preparation of Pt nanoparticles by electrochemical reduction of $Pt(acac)_2$ has been attempted in aprotic bis(trifluoromethylsulfonyl)amide ($TFSA^-$)-based ionic liquids composed of trimethylhexylammonium ($TMHA^+$), and pyrrolidinium cations with different alkyl chain length, 1-butyl-1-methylpyrrolidinium (BMP^+), 1-hexyl-1methylpyrrolidinium (HMP^+) and 1-decyl-1-methylpyrrolidinium (DMP^+). The aim of the present study is to understand the formation mechanism of Pt nanoparticles from $Pt(acac)_2$ and have an insight on controlling the size of the nanoparticles.

Chapter 1 presents a brief description about the metal nanoparticles, ionic liquids and possibility of preparation of metal nanoparticles in ionic liquids.

Chapter 2 describes the general experimental techniques used in the present study.

In chapter 3, electrochemical reduction of $Pt(acac)_2$ has been investigated in $TFSA^-$-based ionic liquids using various electrochemical techniques. $Pt(acac)_2$ was found to exist as a square planer complex in each ionic liquid. $Pt(acac)_2$ was suggested to be reduced to metallic Pt via a two-electron transfer process at a glassy carbon (GC) electrode. Deposition of Pt on a stationary GC electrode was possible by electrochemical reduction of $Pt(acac)_2$ in TMHATFSA and BMPTFSA. In addition, Pt nanoparticles were obtained after cathodic reduction of $Pt(acac)_2$, probably due to the hindrance of the surface process related to electrodeposition by the accumulation of cations of the ionic liquid on the electrode surface.

Chapter 4 is concerned with the investigation of the effect of electrochemical parameters on controlling the size of the Pt nanoparticles prepared by electrochemical reduction of $Pt(acac)_2$ in BMPTFSA, HMPTFSA and DMPTFSA. The average size of Pt nanoparticles prepared by using a glassy carbon rotating disk electrode was found to be independent of the electrode potential, rotation rate or current density. The average size of Pt nanoparticles increased slightly with increasing the alkyl chain length of cations of the ionic liquid, probably related to the stabilization of the Pt nuclei by the ions of the ionic liquids.

Chapter 5 summarizes the present work and describes the perspectives on the control of the size of the metal nanoparticles by careful choice of electrochemical parameters and the ionic liquids.