

Title	Electrochemical studies on platinum
Sub Title	
Author	山本, 博信(Yamamoto, Hironobu)
Publisher	慶應義塾大学藤原記念工学部
Publication year	1965
Jtitle	Proceedings of the Fujihara Memorial Faculty of Engineering Keio University (慶應義塾大学藤原記念工学部研究報告). Vol.18, No.71 (1965.) ,p.75(11)- 76(12)
JaLC DOI	
Abstract	
Notes	Summaries of Doctor and Master Theses Doctor of Engineering, 1965
Genre	Departmental Bulletin Paper
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=KO50001004-00180071-0011

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Electrochemical Studies on Platinum

Hironobu YAMAMOTO*

The thesis consists of two parts. In the first part are presented the results obtained in a series of fundamental studies on oxidation-reduction reaction of platinumchloride complex ions. The latter concerns with the electrode material for electrolytic oxidation which has been developed based on the results of above mentioned experimental studies. The followings are the summary of the thesis.

(I—1) In order to discuss the oxidation-reduction reaction of platinum in Cl^- -containing solutions, standard potentials of platinumchloride complex ions were determined by two different methods. The first method essentially concerns with the equilibrium potential determination of the system PtCl_6^{2-} — PtCl_4^{2-} and it was found that the potential is reproducible when high purity carbon was used as electrode. The other method consists of potentiometric titration of chloroplatinic acid with stannous chloride, from which equilibrium potentials of the systems PtCl_6^{2-} — PtCl_4^{2-} and PtCl_4^{2-} —Pt were determined. Since the standard oxidation-reduction potentials thus obtained in each method showed good agreement and satisfied Nernst's equation, thermodynamic constants of the oxidation reduction reactions were evaluated reasonably.

(I—2) The author studied intermediate products observed during the reduction process of Pt^{2+} with Sn^{2+} , and discussed their structure and decomposition mechanism. It was shown that red anionic complexes having $\text{Sn}^{2+}/\text{Pt}^{2+}$ ratios of 1/2, 1/1, 3/1 and 5/1 were produced temporarily in an inert atmosphere.

(I—3) In an attempt to get well-defined Pt-deposit, several kinds of additives to the chloroplatinic acid bath were tested and sodium sulfate was found to be one of the most effective additives. Optimum operating conditions were determined and recommended base materials were proposed also.

(I—4) The mechanism of cathodic reduction of chloroplatinic ion was analysed by current-controlling polaraization and potential-controlling polarography. It was found that the reduction process could be divided into two stages.

(II—1) Anodic behaviors of several kinds of Pt plated electrode prepared in the above mentioned bath were studied. It was found that the magnetite electrode of which surface was covered with platinum showed excellent anodic behavior, and this electrode was termed "PME."

(II—2) As a basic study for the preparation of PME, the author examined the effect of the surface state of magnetite base on the deposits and also the correlation

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between preparing conditions and anodic behaviors of the electrodes prepared. Surface state of deposit was improved by cathodizing the base material in alkaline solution prior to electroplating. The prospect has been fully clarified that useful electrode material could be developed by this method.

(II—3) In order to understand the mechanism of the cathodizing in the preparation of PME, the author studied the cathodic polarization behaviors of magnetite in solutions at wide range of pH value, and discussed the results referring to the potential-pH diagram of the system $\text{Fe—H}_2\text{O}$, and explained the process by which magnetite is reduced to metallic iron.

(II—4) In an attempt for the industrial service of PME in electrolytic oxidation, PME was employed as anode for the electrolytic production of perchlorate, and anodic behaviors were examined. The observed current efficiency was nearly equal to that of platinum electrode and its surface did not suffer from serious corrosion even after 150 hrs electrolysis.