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学 位 論 文 審 査 の 要 旨

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Formation of Nanostructured Anodic Films on Iron and Their Electrode Applications

（鉄へのナノ構造アノード酸化皮膜の形成と電極応用）

Anodizing of valve metals such as Ti, Nb, Ta, W and Al has become a subject of scientific interest in recent years in view of possibilities to form self-organized nanoporous and nanotubular anodic films on metal substrate. An extension of anodizing process to iron group metals opens the way for applications of nanostructured oxides in cost-effective electrochemical devices such as those used in energy conversion and storage systems. The current thesis focusses on anodizing of Fe and electrochemistry of self-organized nanotubes/nanopores in order to estimate the possibility of application in energy storage devices. The objective of the present study is the fundamental understanding of the growth of anodic nanopores/nanotubes on iron implicating the studies on iron single crystals for evaluation on how the anodic film grows depending on facet index number. The modification of the anodic film growth by addition of an alloying element is studied to the control full transition between nanopores and nanotubes in order to meet the requirements of high surface area for desired applications and physicochemical parameters such as bandgap engineering. Further, the functionality of nanostructured anodic iron oxide films for photocatalytic water splitting and lithium ion battery applications is investigated.

Chapter 1 is general introduction of this theis. Overview of anodizing process and applications of nanostructured anodic films is introduced and the objectives of this dissertation are described. Chapter 2 consists of theoretical and practical details of the techniques used in the present study.

Chapter 3 describes the investigations of the effect of crystallographic orientation of iron on anodizing process. Anodizing of iron (100), (110) and (111) single crystals in mono-ethylene-glycol electrolyte containing 1.5 mol dm^{-3} water and 0.1 mol dm^{-3} ammonium fluoride leads to formation of anodic nanopores/nanotubes where the nanopores are essentially composed of oxide nanotubes separated by iron fluoride cell boundaries. It was found that nanoporous/nanotubular film formation apparently depends on the index number of facets on which the anodic film is formed. The film formation on (100) facet is associated with extended gas evolution upon anodizing and consequently corresponds to a shift of current-time curve towards higher current density values comparing with those formed on higher index number facets. The nanotubes formed on (100) facet have a general chemical formula of $Fe_2O_3{\cdot}FeF_2$, whereas those formed on higher index number are composed of $Fe_3O_4{\cdot}FeF_2$. The anodic films formed on Fe (110) and Fe (111) are essentially amorphous whereas that formed on (100) facet shows high degree of crystallinity. The results are discussed in view of anisotropic properties of iron.

In Chapter 4, the effect of alloying of sputter-deposited Fe with 9 at.% tungsten on the growth of nanoporous anodic oxide was studied in mono-ethylene-glycol electrolyte containing 0.1 mol dm^{-3} ammonium fluoride and 1.5 mol dm^{-3} water. The classic nanoporous anodic film (Al_2O_3-like) was developed on pure Fe, whereas the transition of nanopores to nanotubes (TiO_2-like) was observed for anodizing of Fe-W alloy. Both nanoporous/nanotubular anodic films grew in line with the field assisted flow model

with a few fundamental details: i) transition of nanopores to nanotubes was observed upon anodizing of Fe-W alloy, ii) significant reduction of the cell size (nanotube diameter) was obtained on Fe-W alloy, iii) chemically modified layer was developed was produced at Fe-W alloy/oxide interface after anodizing. The primary reason of this transition to nanotubes as well as chemical changes is discussed in view of effective modification of the cell boundary region with tungsten species, probably WF_6 compound, upon growth of anodic film under influence of high electric field strength. Alloying of iron is one of the effective ways to modify the nanostructure of the anodic film on iron.

In Chapter 5, the functionality of Fe-W oxides as photoanode was demonstrated. The nanotubes-type film with 800 nm-thickness and barrier-type film with 540 nm-thickness were grown by modifying anodization conditions, including the water content and anodizing time. Then, the anodic films were annealed at 300 - 400 °C for 30 min to form crystalline structures. The thermal treatment enhanced the crystallinity of the films. The photocatalytic activity of Fe-W oxides was compared with that of Fe oxides, and it was found that the performance was highly enhanced by the addition of tungsten. The possible explanation of the enhanced activity is the efficient separation of the photoinduced electron–hole pairs and large surface area of the uniform nanotube arrays.

The performance of anodic films grown on iron for lithium ion battery application was examined and the resuls were summarized in Chapter 6. The iron oxide nanotubes were synthesized by anodizing of polycrystalline iron in mono-ethylene-glycol electrolyte containing 0.1 mol dm^{-3} ammonium fluoride and 1.5 mol dm^{-3} water followed by thermal treatment at 350-500°C in order to control the crystallinity of the oxide. An increase of crystallinity, the change of the ratio of hematite (Fe_2O_3) to magnetite (Fe_3O_4) and the elimination of fluoride ions were observed with an increase in annealing temperature. The differential capacity plots of $dQ \cdot dE^{-1}$ revealed quasi-reversible lithiation/delithiation process through Li_2O formation. The anodic nanotubes/nanopores annealed at 500 °C provided relatively high areal capacity of 3.5 mA h cm^{-2} at a charge/discharge current density of 20 μA cm^{-2}. The better electrochemical performance was found for nanotubes/nanopores having higher degree of crystallinity, high ratio of hematite (Fe_2O_3) to magnetite (Fe_3O_4) and eliminated fluorides. The cycling stability tests supported with optical microscopy observations of the negative electrode assembled in electrochemical cell for *in situ* measurements indicated adhesion problems and gradual degrease of rate capability mainly caused by the detachment of oxide.
Finally, the main findings of this dissertation are summarized, and future prospects are given in Chapter 7.

Considering these research achievements, we conclude that the author is eligible to receive a doctoral degree of engineering from Hokkaido University.