審 査 の 結 果 の 要 旨

アハマディ ダリアケナリ アハマド
氏　名　Ahmadi Daryakenari Ahmad

Electrophoretic deposition of carbon nanostructured catalyst supports for anode electrodes used in direct ethanol fuel cells

PhD thesis defended by Ahmadi Daryakenari Ahmad

Production of electricity from a renewable fuel is of paramount importance for our society. One possible strategy to contribute to this paradigm shift is to replace fossil fuels with ethanol, a safe and renewable fuel. Electrical work can be produced by electro-oxidation of ethanol in a fuel cell. This type of fuel cells (direct ethanol fuel cell) working at low operating temperature with a safe fuel can be made small enough for mobile applications such as portable electronic equipment. AHMADI developed a solution-based deposition technique of carbon-nanostructure layer serving as a catalyst support for direct ethanol fuel cells and investigated the fabricated nanostructure layer performance in ethanol electro-oxidation. AHMADI main goal is to develop a fabrication technique for an anode electrode of direct ethanol fuel cells without resorting to expensive manufacturing processes and catalyst materials made of precious metals. AHMADI proposes to obtain catalytic NiO nanoparticles loaded on a mesoporous carbon layer by electrophoretic deposition of a colloid consisting of graphitic flakes dispersed with NiO nanoparticles. That is, the electrophoretic process is a fast-growth-rate and single-step process in which the catalyst support and the catalyst are deposited concurrently.

The manuscript consists of five chapters.

The first chapter gives an introduction to the field. The advantages of direct ethanol fuel cells are first given. Then the techniques used in the fabrication of electrodes are reviewed with emphasis on the deposition of catalyst supports. Two strategies are given, namely, co-deposition of the catalyst support together with the catalyst materials and subsequent deposition of the catalyst layer onto which catalyst is deposited. The latter is suitable for noble metal as it uses low amount of materials and is known to deliver large mass activity. The former should be used with non-noble metal as the catalyst material amount is large. Electrophoretic deposition is introduced as a possible technique to obtain catalytic nanoparticles loaded on a mesoporous catalyst support. The choice of materials for ethanol oxidation is presented and the general structure of the manuscript given. The deposition of the catalyst support using graphitic flakes is first presented and the obtained catalyst layer evaluated in ethanol electro-oxidation after palladium catalyst was sputtered on the catalyst support. The optimum fabrication conditions are used to study the co-deposition of graphitic flakes and NiO nanoparticles and finally the electro-oxidation mechanism is elucidated.

Chapter two reports the fabrication technique and optimization of the catalyst support layer. The catalyst support layer is obtained using DC electrophoretic deposition from a colloid consisting of nanographitic flakes dispersed in isopropyl alcohol together with magnesium ions. The magnesium ions control the flake surface charge in the colloid and are used to bind nanographitic flakes together. The packing density and conductivity of the deposited layer are controlled by the ion concentration in the colloid. The performance of the catalyst support was first evaluated by decorating the fabricated catalyst support layers with palladium nanostructures serving as the catalyst (palladium is thought as a replacement for the standard platinum catalyst). The fabricated support layer with the highest packing density exhibited improved conductivity and electro-oxidation performance reaching 1.5 A/cm^2 per mg of palladium. This performance is among the best for direct ethanol fuel cells based on palladium.

Chapter three reports the co-deposition of the catalyst support together with non-precious metal catalyst nanoparticles. Using the optimized fabrication conditions for packing density of the catalyst support, the deposition of a non-precious metal catalyst together with its catalyst support in a single-step electrophoretic deposition is demonstrated. The catalyst consists of nickel oxide nanoparticles which are attached on the surface of the nanographitic flakes during the electrophoretic process. The fabricated anode showed a very low onset voltage for the electro-oxidation of ethanol. However, the anode stability at constant voltage was not satisfactory. Furthermore, a better control of the dispersion of the catalytic nanoparticles on the catalyst support is demonstrated using pulsed electrophoretic deposition. Using short pulses help to decrease agglomeration of catalytic nanoparticles on the nanographitic flake support and form well dispersed catalytic particles on the support. As a result of the improved dispersion of the catalytic nanoparticles, a larger electro-oxidation current was achieved. It should be noted that if AHMADI results compared well with results reported in the literature in terms of the onset voltage and maximum current, the stability of the fabricated electrode still remains a challenge.

Chapter four clarifies the mechanism for ethanol electro-oxidation on nano-graphitic flakes support loaded NiO nanoparticles. To clarify the mechanism, the sample is first modified by annealing (or plasma treatment) to obtain a different electrochemical behavior, then the samples properties such as material characteristics, kinetics of the electrochemical reactions and conductivity are compared for samples without and with annealing. Temperature dependence measurements indicate a charge transport mechanism based on hopping transport, which is changed to drift transport for the annealed sample. The hopping charge transport is related to the appearance of an ethanol electro-oxidation current peak at low voltage, which is different from the reported literature data.

The conclusions of the manuscript are given in Chapter five. The major advantages of the proposed electrode are two folds, namely, ease of fabrication which does not resort on vacuum technology to obtain the catalyst and its support and low cost of the electrode layer which uses non precious metal as catalyst (i.e. NiO). This type of electrode is intended for use in room-temperature small fuel cells which are used to operate personal computers and other mobile electronic devices. These fuel cells are not hazardous because they operate on ethanol and provide electricity from a sustainable energy source.

AHMADI delivered one publication in a per-reviewed international scientific journal.

よって本論文は博士（工学）の学位請求論文として合格と認められる。