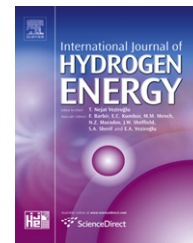


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Electrical and thermal transport properties of vanadium oxide thin films on metallic bipolar plates for fuel cell applications

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ABSTRACT

We have focused on the in-depth comparative evaluation of the suitability of electrically-induced thermal transport characteristics of highly disordered vanadium oxide thin films deposited onto metallic bipolar plates as an expeditious self-heating source for the successful cold-start of fuel cells in a subfreezing environment. To achieve this, sol-gel derived vanadium oxide thin films on the non-polished surface of 316L austenitic and 446M ferritic substrates have been fabricated by a dip-coating process. The effects of electrical properties on thermal energy dissipation rate of the as-synthesized thin films deposited onto 316L and 446M stainless steel plates were firstly investigated and compared with each other. Subsequently, a series of physical, chemical, and structural analyses of the thin films have been performed using several analytical techniques such as the ASTM D3359, the ASTM D5946, XPS, and FE-SEM. The most important finding of this study was that the electrical resistivity of the thin films on 446M ferritic substrate was extremely low on a level of 4.8% of the 316L sample at $-20\text{ }^{\circ}\text{C}$, and then the surface temperature rise of the thin film on 316L austenitic substrates was approximately 21.8 times greater than that of 446M ferritic substrates under simulated cold starting conditions (i.e., at a current density of $0.1\text{ A}\cdot\text{cm}^{-2}$ at $-20\text{ }^{\circ}\text{C}$). Therefore, we concluded that vanadium oxide thin films on 316L austenitic stainless steel plates appears to be more applicable than those of 446M ferritic substrates for the cold-start enhancement of fuel cells from the practical point of view.

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1. Introduction

The need for a more environmentally friendly and efficient energy conversion device has led to an intensive interest in fuel cell research in the past decades, particularly polymer electrolyte fuel cells (PEFCs). To date, PEFCs have emerged as the most promising alternative power source for eco-friendly automotive applications that have the potential to replace existing internal combustion engines. However, the commercialization of PEFCs for vehicular power systems still faces several challenging technical issues such as

performance, stability, and reliability in the frigid and severe cold climate conditions (i.e., cold-start capability). It is practically recognized that cold-start capability and survivability of PEFCs in subfreezing environments is of extremely importance to achieve the long-term reliability and guaranteed performance of automotive fuel cell engines. During the cold-start operation of PEFC engines, produced water by the electrochemical reactions in membrane electrolyte assemblies (MEAs) might freeze instantaneously at the reaction sites and hinder the reactant transport from gas channels through catalyst layers due to the ice-filled pores and the ice-covered

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active surfaces as shown in Fig. 1, resulting in the drastic performance degradation of fuel cell systems. In addition, these cold-start phenomena might induce aging acceleration of MEAs, which is due mainly to the structural damage by repeated volumetric displacement of water under freeze/thaw cyclic conditions. Therefore, either an internal or external heat supply available to overcome the formation of ice at subzero temperatures is one of the significant considerations for the successful cold starting of PEFC automotive engines.

Earlier studies focused exclusively on external heating methods (e.g., coolant heating, the blowing of hot air, and thawing tank) for thaw-heating at start using adaptive fuzzy logic control of PEFC systems [1–7]. Despite the fact that these methods have been very effective in improving cold-weather driving performance and the cold-start capability of fuel cell vehicles at subfreezing temperatures, they require significantly higher amount of electrical energy for warm-up occasionally. Therefore, a new concept of cold-start strategy possible to supply heat at sub-freezing temperatures is needed to minimize relatively the parasitic losses compared with the conventional methods. For this reason, more recently, researches on more energy-efficient alternative methods have been attempted by a number of groups with the common goal of better understanding cold-start phenomena in PEFCs and improving thaw-at-start of fuel cell systems, both numerically [8–15] and experimentally [16–23]. Although considerable efforts for freeze-thaw management in PEFCs have been devoted to developing the technical solutions for the rapid cold startup of fuel cell vehicles, little has been reported in academic journals. Among the related literature, notable experimental studies proposing promising solutions to the PEFC freeze problem for the cold-start enhancement of PEFCs have been conducted by Kagami et al. [24], St-Pierre et al. [25], Cho et al. [26], and Jung and Um [27]. Kagami et al. found that the self-starting of PEFCs could be possible above ambient temperatures of $-5\text{ }^{\circ}\text{C}$, whereas external heat supply should be needed for ice melting in the catalyst layer below $-5\text{ }^{\circ}\text{C}$. St-Pierre et al. and Cho et al. investigated that the solution-purging method could be used

to prevent the performance degradation of PEFCs by purging the fuel cells with an antifreeze solution (i.e., methanol, ethanol, ethylene glycol, and isopropanol) whose freezing temperature is much lower than $0\text{ }^{\circ}\text{C}$. Jung and Um demonstrated that thermal dissipation characteristics of crystalline vanadium oxide thin films deposited onto 316L stainless steel bipolar plates could be effectively used as a self-heating source to melt frozen water at subzero ambient temperatures. In a precedent specific case study, they showed that a temperature rise of the multilayer vanadium oxide thin films induced by significant Joule heating was approximately $41.65\text{ }^{\circ}\text{C}$ at a current density of 0.1 A cm^{-2} at $-20\text{ }^{\circ}\text{C}$.

The present study is to extend the previous research of the authors [27], by concerning the effective use of the self-sufficient heat dissipation of vanadium oxide thin films coated onto the flat surface of 316L stainless steel bipolar plates for improving thaw-at-start. To complement the previous works on the applicability of vanadium oxide thin films on metallic bipolar plates in subzero conditions, it is necessary to evaluate the effect of material characteristics of different types of metallic bipolar plates (i.e., austenitic and ferritic stainless steels) on thin-film properties (i.e., physico-chemical properties) of oxidized vanadium. Based on the aforementioned purpose, we performed a comparative study on electrically-induced thermal transport characteristics of crystalline vanadium oxide thin films deposited onto 316L austenitic and 44M ferritic stainless steel bipolar plates as typical examples of the most commonly used metallic materials under simulated cold-start conditions of fuel cells. Subsequently, applicability and thermo-physical properties of the as-deposited crystalline thin films on both substrates at sub-freezing temperatures were evaluated and compared by directly measuring temperature dependent electrical properties and time-resolved temperature evolution of the samples. In addition, a series of interfacial, structural, and chemical analyses were conducted to measure the adhesion, equilibrium water contact angle, surface energy, microstructure, and chemical compositions of the vanadium-based thin-film layers.

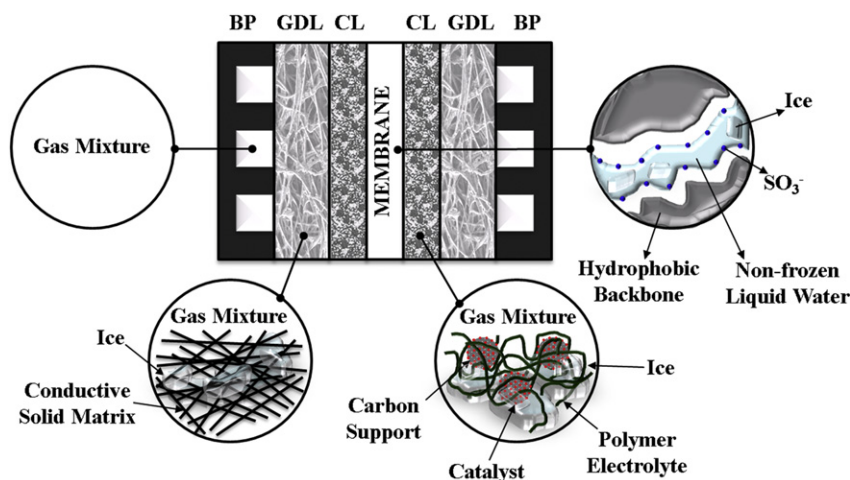


Fig. 1 – Schematic illustration of various formation of water in fuel cells at subzero temperatures. BP, GDL, and CL indicate bipolar plate, gas diffusion layer, and catalyst layer, respectively.

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