



# Synthesis, characterization, and transport properties of single-layer pure and molybdenum-doped vanadium oxide thin films on metallic conductive substrates



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## ABSTRACT

Single-layer undoped and 10 mol% molybdenum (Mo)-doped vanadium oxide ( $V_2O_5$ ) thin films with thicknesses of approximately 342 nm are fabricated by an aqueous sol-gel method and then deposited onto 316L stainless steel conductive substrates. The influence of various annealing temperatures (in a nitrogen atmosphere) on the structural and electrical properties of undoped and Mo-doped vanadium oxide thin films is investigated. Through a controlled annealing process, the electrical resistances of the single-layer thin films are optimized to attain the required amount of Joule heating for cold-start fuel cell applications within an ambient temperature range (273.15 to 253.15 K). The films show a negative temperature coefficient (NTC) behavior and a transition from a metal to an insulator at sub-zero temperatures. The highest electrical resistivities are measured to be  $0.032 \Omega \cdot \text{cm}$  and  $0.071 \Omega \cdot \text{cm}$  for undoped and Mo-doped vanadium oxide films, respectively, after annealing under 20 sccm  $N_2$  at 673.15 K. Consequently, the equilibrium surface temperature of the single-layer Mo-doped vanadium oxide thin film increases from 253.15 K to 299.46 K upon induced Joule heating at a current density of  $0.1 \text{ A} \cdot \text{cm}^{-2}$ . Thus, it is concluded that single-layer NTC Mo-doped vanadium oxides can be effectively used for cold-start fuel cell applications.

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## 1. Introduction

Many experimental investigations on the freeze/thaw development of PEFCs have been performed; however, further efforts to understand the physics of cold-start are needed due to its importance in PEFC deployment. Hishinuma et al. [1] experimentally investigated the performance of a single cell in a sub-zero temperature environment. They concluded that the self-startup of PEFCs below  $-5^\circ\text{C}$  was not possible without external heat assistance. McDonald et al. [2] experimentally analyzed the physical changes in fuel cell membranes caused by freeze/thaw cycling. They performed the experiment with 385 temperature cycles (between room temperature and  $-40^\circ\text{C}$ ) on PEFCs over a period of three months. Cho et al. [3] conducted an experimental study on fuel cell degradation associated with thermal cycling. They operated fuel cells at an initial temperature of  $80^\circ\text{C}$ , cooled the cells to sub-zero temperatures, and then returned the temperature to  $80^\circ\text{C}$  to begin another thermal cycle. They observed the degradation of the fuel cells, which was attributed to frozen water that remained in the PEFCs after shutdown. Oszcipok et al. [4] conducted single-cell isothermal cold-start measurements. They studied the performance variation of a single cell under different operating conditions and found that the membrane

humidity was increased by the water produced at subfreezing temperatures; ice was formed when the produced water flowed through the gas diffusion media and the catalyst layers. Yan et al. [5] conducted experimental investigations using a  $25 \text{ cm}^2$  cell. They studied the cold-start behavior of fuel cells and found that there was an irreversible performance loss when the cell temperature fell below  $-5^\circ\text{C}$ . He et al. [6] presented a one-dimensional transient model to demonstrate the ice-lens formation and water migration process during low temperature operations of fuel cells. Khandelwal et al. [7] and Jiao et al. [8] developed a one-dimensional thermal model and investigated the cold-start performance of PEFCs and the corresponding energy requirement at various ambient conditions. They recommended that purging of heated coolant above  $0^\circ\text{C}$  was an efficient way to achieve rapid PEFC cold-start. Wang and Wang [9,10] and Mao and Wang [11] developed a transient computational model of PEFC operation and a multi-dimensional model by incorporating tools of ice formation, respectively. Mao and Wang [11] analyzed the influence of membrane thickness and startup current density on cell performance during cold-start. Ahluwalia and Wang [12] refined a simple two-dimensional model of a single cell for simulating the cold-start of PEFCs. It was concluded that preheating the supply gases and electrically heating the cell stack could produce only small effects on the ability of PEFC to self start.

Despite the substantial previous research on the cold-start of fuel cells, studies of the internal heat supply strategies have been limited.

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One such study was conducted by Jung et al. [13,14], who introduced an alternative internal self-heating method for the cold start-up of fuel cells that minimized the parasitic power loss relative to external heating methods. They applied thin coatings of negative temperature coefficient (NTC) materials onto bipolar plates (BPs), allowing Joule heating to be induced through the films. The Joule heating then allowed heat to be dissipated into fuel cells at sub-zero temperatures. In their work, the specific resistance required to generate the necessary Joule heating was theoretically deduced to allow for proper thermal management.

Among the various NTC materials, vanadium oxide and its compositions can be utilized as potential heat generation substances due to their structural flexibility, thermal stability, affinity to other materials, resistance to many chemicals, and outstanding electrical properties. Moreover, the electrical transport properties of vanadium oxides can be modified for cold-start PEFC applications by adding suitable dopants and/or changing the processing conditions (e.g., ambient gas flow rates and annealing temperatures) [15–17]. Molybdenum has been found to be a suitable dopant into vanadium oxides for a wide range of applications because of their selective oxidation states. It should be noted that there are unique interactions between vanadium oxides and molybdenum oxides owing to the similarity of the ionic radii and structures in their highest oxidation states [18,19]. This should be useful for the formation of solid solutions with different oxidation states, which are beneficial to tuning electrical properties of vanadium oxides at any required temperature range [20].

Considering many challenges for the commercialization of fuel cells [21], new materials for PEFC cold start applications are being developed through various fabrication techniques to reduce fuel cell cost. Among various wet chemical deposition techniques, sol–gel dip coating is a cost-effective method for facile fabrication of large substrates and can offer some technical advantages such as low processing temperatures, well-controlled film compositions, and better homogeneity of final solids for prospective engineering applications.

The purpose of this study is to investigate the possibility of modifying the electrical transport properties of single-layer thin films on metallic conductive substrates (i.e., BPs). To achieve this goal, single-layer pure and Mo-doped vanadium oxide thin films are prepared using a sol–gel dip coating method, and a series of measurements are conducted (over a temperature range of 273.15 to 253.15 K) to monitor the electrical transport properties of the oxide films as a function of the annealing conditions. The influence of the Mo dopant on the electrical transport properties of vanadium oxide films is discussed. In addition, the electrical transport properties and microstructures of pure and Mo-doped vanadium oxide thin films are compared under a series of annealing conditions. This study provides a physical understanding of the electrical transport properties of single-layer undoped and Mo-doped vanadium oxide films. We also demonstrate a method that can be used to manipulate these materials to provide a new cold-start strategy for PEFCs.

## 2. Experimental

### 2.1. Sol–gel synthesis

In the present study, commercially available vanadium oxytriisopropoxide ( $C_9H_{21}O_4V$ , Sigma-Aldrich), which is soluble in a variety of organic solvents, was used as a precursor. 2-Propanol (anhydrous 99.5% PriOH, Sigma-Aldrich), which is the primary alcohol of the vanadium alkoxides, was used as a diluent. The vanadium-containing solution was synthesized by mixing vanadium oxytriisopropoxide, 2-propanol, and acetyl acetone (used as a chelating agent) in an inert environment and stirring the resulting vanadium solution for at least 2 h to create a homogeneous mixture. This novel sol–gel synthesis method was used to prepare the Mo-doped vanadium oxides in the present study. Stoichiometric amounts of commercial vanadium oxytriisopropoxide ( $C_9H_{21}O_4V$ , Sigma-Aldrich) and molybdenum

isopropoxide ( $C_{15}H_{35}MoO_5$ , Sigma-Aldrich) were mixed, and the synthesis route followed the sequence shown in Fig. 1. All of the Mo-doped  $V_2O_3$  films were prepared with 10 mol% Mo (unless otherwise noted).

### 2.2. Sol–gel dip coating of thin films

Samples of flat stainless steel plates were dip-coated using a hoisting device (i.e., a computer-controlled precision dip-coater, Jaesung Engineering Co. Model. No. ZID-3, Ansan, Gyeonggi-do, South Korea). The coating thickness was controlled by the concentration of the solution, and the samples were coated at a hoisting speed of  $5 \text{ mm s}^{-1}$  using a programmed DC motor in a completely sealed chamber under ambient conditions. The coated specimens were then dried at approximately 353.15 K in an inert atmosphere using a halogen lamp to remove excess solvent. The fabrication and annealing procedures were performed more than five times for each film to ensure repeatability of our experiment. Typical experimental conditions for dip-coating are presented in Table 1.

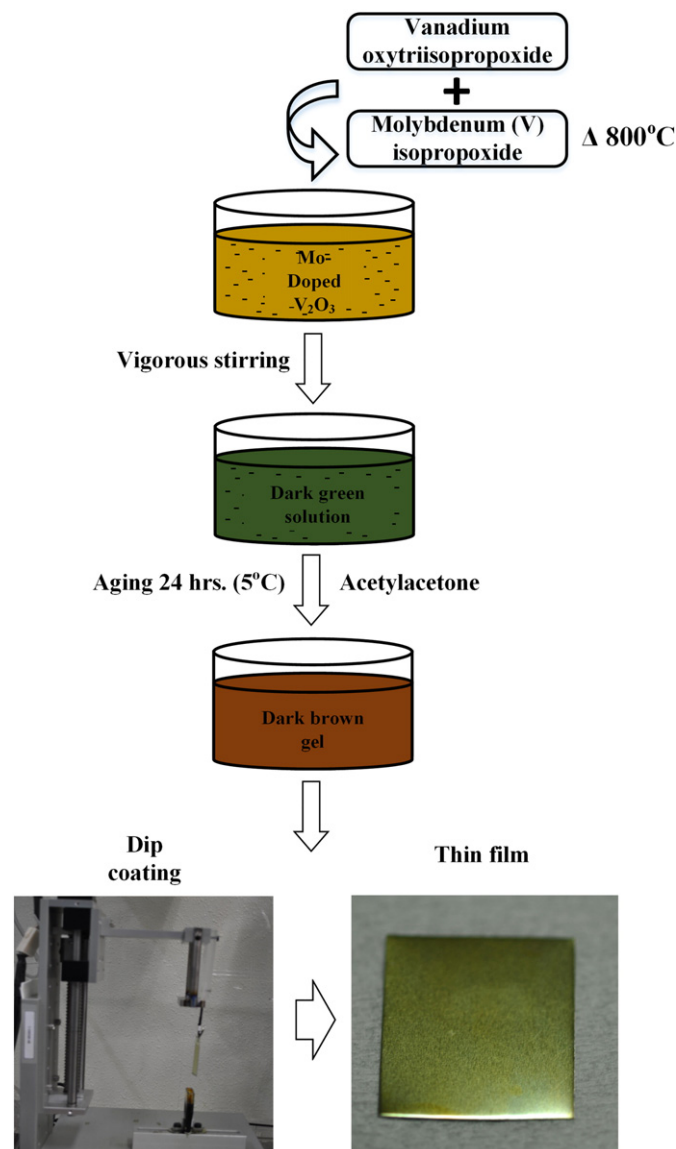


Fig. 1. Schematic diagram of the Mo-doped vanadium oxide sol gel synthesis for dip coating.

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