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Carbon monoxide tolerant platinum electrocatalysts on niobium doped titania and carbon nanotube composite supports

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HIGHLIGHTS

- Material characterization reveals structure and property of electrocatalysts on differing supports.
- Carbon composite supports with doped titania can improve CO tolerance of platinum catalysts.
- Hydrogen pumps are used to effectively qualify electrocatalyst behaviors in the anode of MEAs.
- Niobium doped titania supports showed resilient performance in hydrogen pump tests with CO.

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ABSTRACT

In the anode of electrochemical cells operating at low temperature, the hydrogen oxidation reaction is susceptible to poisoning from carbon monoxide (CO) which strongly adsorbs on platinum (Pt) catalysts and increases activation overpotential. Adsorbed CO is removed by oxidative processes such as electrochemical stripping, though cleaning can also cause corrosion. One approach to improve the tolerance of Pt is through alloying with less-noble metals, but the durability of alloyed electrocatalysts is a critical concern. Without sacrificing stability, tolerance can be improved by careful design of the support composition using metal oxides. The bifunctional mechanism is promoted at junctions of the catalyst and metal oxides used in the support. Stable metal oxides can also form strong interactions with catalysts, as is the case for platinum on titania (TiO_x). In this study, niobium (Nb) serves as an electron donor dopant in titania. The transition metal oxides are joined to functionalized multi-wall carbon nanotube (CNT) supports in order to synthesize composite supports. Pt is then deposited to form electrocatalysts which are characterized before fabrication into anodes for tests as an electrochemical hydrogen pump. Comparisons are made between the control from Pt-CNT to Pt-TiO_x-CNT and Pt-$Ti_{0.9}Nb_{0.1}O_x$-CNT in order to demonstrate advantages.

1. Introduction

Electrocatalysts are an essential part of many electrochemical cells which are often assembled in challenging ways to design the most effective electrodes. Unfortunately, catalysts such as platinum (Pt) are expensive and often contribute substantially to the overall system cost. To reduce the amount needed, nanostructured Pt particles can be supported on conductive substrates that are intricately distributed into electrodes used for polymer electrolyte cells. In the anode of a fuel cell, the overpotential for oxidation of hydrogen (H_2) is relatively low when compared to the oxygen reduction reaction (ORR) of the cathode. However, presence of carbon monoxide (CO) in the hydrogen oxidation reaction (HOR) has a significant poisoning effect under typical operating conditions when active Pt sites become covered during exposure. At operation temperatures <100 °C, even low concentrations $\gtrsim 10$ ppm CO can severely impact cell performance in a short time [1–3]. Electrode poisoning from CO in the fuel is one of the major challenges plaguing development of this technology. Therefore, a more resilient electrocatalyst in operations with CO can have very significant cost savings and deserves our attention [4].

Electrocatalyst properties of metals can depend on crystalline epitaxy, lattice strain, metal-ligand effects, and from their interfaces with adjoining compounds that could be a constituent phase of the support [5,6]. Although it is possible to alter the adsorption properties of CO on electrocatalysts by changing these parameters, the bifunctional mechanism has been well established for its removal once poisoned [7,8]. In the case of adsorbed CO on

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the catalyst, most is converted to carbon dioxide (CO_2). This effect is promoted when dually adsorbed species are involved in its oxidation as shown by Langmuir–Hinshelwood type reaction of Equation (1). Metal oxide (MO_x) phases formed in proximity to catalysts can serve this purpose by analogous ways to alloys with Pt [5,9]. Construction of a catalyst support with these materials could aid this property in addition to making it more durable.

$$MO_x - OH + Pt - CO_{ad} \rightarrow CO_2 + Pt + MO_x + H^+ + e^- \qquad (1)$$

Improving tolerance to CO has been extensively investigated through alloying Pt with less-noble elements to promote bifunctional effects, although alloys can be limited by their stability. Advances with Pt alloys containing promoters such as Ru, Sn, and Mo are considered a state-of-the-art for CO tolerance, but these metals can also become compromised during operations [10–15]. From the perspective of stability, it is probably more rational to prepare those metals initially in a preferred oxidation state that form junctions with Pt [16–18]. In any case, contamination from the fuel adsorbs on anode catalysts; to restore their activity, oxygen pressure, temperature, and/or cell potential are generally increased to accomplish removal [19–21]. However, these processes can result in irreversible oxidation of the electrocatalyst as well. Unintended fuel starvation and cell reversal can also lead to high potentials, low pH, and conditions that cause degradation of this electrode [11,22,23]. These events all result in the loss of performance from electrocatalysts which can be corroded similarly to catalysts in the cathode of the fuel cell [24]. Electrocatalyst losses may be measured by changes in reversible features from cyclic voltammetry which correlate with active sites [25]. In alloys with Pt, the more active metal tends to be sacrificed while passivation occurs on the surface and noble metal lattice strain gets relieved [14,26]. Catalyst activity is lost, but secondary symptoms originating from this issue may also persist. For example, dissolved cations from alloyed metals can diffuse through proton channels and plate out in the electrolyte or other undesirable places [11,13]. Electrocatalyst degradation has a cumulative effect on performance which can eventually kill the cell; this paradox poses a challenge to the purpose of same materials which also make them work so well [27]. In the anode, tolerance to CO contamination should come without a big cost to stability for ideal electrocatalysts.

Electrocatalysts must be validated in electrodes with conditions similar to those found in real applications. Half-cells and rotating disk electrode (RDE) studies are essential in understanding fundamental behaviors to guide specific design, but results from full cell hardware are necessary in confirming the effectiveness of working electrodes. However, fuel cell testing complicates understanding of anode behavior due to sluggish ORR and other cathode effects. Electrochemical hydrogen pumps can provide more accurate characterization of the anode oxidation reactions. Protons formed in the anode are simply pumped across the membrane electrode assembly (MEA) and reduced at the cathode by applying potential. For the reference electrode, Pt black electrocatalysts dually serve as a cathode in the fast hydrogen evolution reaction. More sophisticated designs of this type can also efficiently serve an important role to purify diluted process flows and pressurize clean H_2 gas which is ideal for fuel cells. Application of potential provides for characterization of catalysts by a cyclic voltammetry technique which can be performed similarly to the hydrogen pump, except fuel has been purged from working electrodes by inert gas. From a diagnostic perspective, losses in pump performance and overpotentials can be relatively easy to quantify.

Transition metal oxides selected for this study were carefully chosen for stability and their interaction with Pt catalysts. The abundant element titanium (Ti) was picked as the major constituent with a minor addition of niobium (Nb) included as an electron donor in the oxide matrix. Both oxides have a wide passivation region overlapping the operating ranges used in the environment of related electrochemical cells, based on equilibrium Pourbaix (E_h-pH) diagrams [28,29]. It is imperative that materials used in catalysts should at least be prepared near to their equilibrium state (e.g. TiO_2 or Nb_2O_5) or else their surfaces will eventually adopt it during operations, resulting in irreversible transformations. The metal oxides are intended to serve several functional roles in the support. Titania can provide a stronger interaction with catalysts than carbon, improving durability by limiting diffusional growth [30–33]. The noble catalyst can also reduce the support metal oxidation state to form oxygen vacancies near the surface which facilitate the formation of hydroxyl (–OH) groups from the dissociation of water [34–38]. Titanium dioxide has been used for numerous catalytic applications and the science of its surface chemistry has been the single most investigated among transition metal systems [39,40]. In electrocatalysis, high conductivity is a necessary requirement and inadequate conduction of metal oxides has limited their use as support in related applications at low temperature. Although, an extensive number of recent reports have emerged which indicate there can be a synergistic combination for benefits to activity and stability from metal oxide supported electrocatalysts. Solely using metal oxide phases alone for the support is perhaps not practical because long range order of larger doped crystals (e.g. rutile) is typically needed to effectively form conductive electronic pathways, but the use of large crystals comes with a cost to available surface area [41–43]. Nevertheless, using metal oxides in conjunction with carbon could still be an effective approach to maintain suitable conductivity in the electrode without requiring a high catalyst loading [44–57]. Therefore, it is a goal to translate these conceivable developments into results that can be established in electrodes of low temperature cells.

The choice of doped metal oxides for this research is based on defect engineering principles that should be favored in the environment of the electrode. Defects are formed in host crystals by including irregular placement of elements that add charge carriers, often found in the gap state of oxides. Titanium (IV) dioxide has a wide band gap, but can be reduced by extra electrons formed during loss of oxygen atoms in the compound and it is typically referred to as n-type semiconductor. Adding defects contributes to both electron acceptor and donor properties, but often one type dominates. The selection of Nb as a donor dopant for Ti is based on its ionic radii, coordination number, and preferred valence state in the environment. Donor doping is ideal in reducing environments based on laws of mass action as suggested by the relationship of Equation (2) in Kröger–Vink notation [58,59]. At low oxygen concentrations found in the anode, oxygen vacancies ($V_O^{\bullet\bullet}$) are compensated by electron carriers as represented by the reaction of Equation (3). When Nb^{+5} is reduced to Nb^{+4}, an electron on ($Nb_{Ti}^{\bullet}$) is formed as a shallow donor in titania [60,61]. Solid oxide fuel cells rely on these defect relationships for conductivity, where defects are more mobile at higher temperature. At lower temperatures, defects may become quenched in the lattice and considered as a quasi-equilibrium that can contribute to new mobility states though bulk diffusion is reduced [62–66]. Only a few other stable elements with higher oxidation are suggested as donors in titania; among these are Nb (V), Ta (VI), and W (VI) oxides found at high potentials ~1 V and in very low pH values often found in electrochemical cells with acidic electrolytes based on proton exchange [28]. Importantly, the oxides of positive transition metals have a tendency to form oxygen vacancies and hydroxides at their surface when reduced through strong interactions with more electronegative metal clusters deposited on them [67]. Substitution limits for