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The role of electronic properties of Pt and Pt alloys for enhanced reformate electro-oxidation in polymer electrolyte membrane fuel cells

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ABSTRACT

One major challenge of PEM fuel cells development is to overcome the activity and durability issues o the current anode materials which are susceptible to hydrogen impurities. To design stable and efficient catalysts with enhanced reformate tolerance, a comprehensive understanding of the underlying mech-anisms is crucial. In this work, the CO and CO_2 tolerance of a series of Pt-based catalysts are tested in a PEM fuel cell. We report that the CO tolerance is the highest for PtMo/C followed by PtCoMo/C, PtRuMo/C PtRuPb/C, PtRu/C, PtCo/C, PtFe/C, PtNi/C and Pt/C; while the CO_2 tolerance increases in the order: PtCo PtNi> PtRuPb> PtRu> PtCoMo> PtRuMo> PtFe> Pt> PtMo. In situ XAS measurements in combination with FEFF8 calculations are performed to correlate the CO and CO_2 tolerance trends with the electronic prop-erties of these Pt-based alloy catalysts. We find that the anode overpotential in the presence of CO_2 can be generally related to the experimental Pt d-band vacancy or calculated d-band center, and thus governed by the Pt electronic properties modified by the alloyed metal(s). No such correlation is observed between the anode overpotential in the presence of CO and Pt electronic properties, which highlights the key roles of Mo or Ru in improving CO tolerance via promotion and bifunctional mechanisms. Building upon these results a new ternary alloy PtCoMo/C was synthesized. This electrocatalyst shows the best reformate tolerance in low temperature PEM fuel cells by taking advantage of the bifunctional mechanism induced by Mo and the ligand effect induced by Co simultaneously. Our findings put forward a theory which gives a strong perspective for further research and development of new inexpensive catalysts with superior CO tolerance and durability.

1. Introduction

Reformate as the PEM fuel cells anode side feedstock, typically contains a mole fraction of hydrogen in the range of 0.4–0.75, with CO in the range of 50–100 ppm and CO_2 making up the balance. CO is well-known as a poison for hydrogen oxidation on platinum in the anode of a PEM fuel cell and a medium temperature phosphoric acid system. Besides, CO_2 has the potential of CO production through either (a) a reverse water gas shift reaction [1–5] ($CO_2 + H_2 \leftrightarrow CO + H_2O$) that is the reduction of CO_2 at the operating temperature of PEM fuel cells of 80 °C or (b) the electro-reduction of CO_2 through $CO_2 + 2M\text{-}H_{ads} \leftrightarrow M\text{-}CO_{ads} + H_2O + M$ [6–8]; The poisoning level caused by CO_2 is beyond those accounted for by simple dilution [2–5]. Hence, on the way to develop new durable catalysts for impure hydrogen feedstock, the enhancement of the reformate oxidation should be considered over the whole range of industrial CO and CO_2 concentrations. PtRu alloy catalyst has been widely acknowledged as one of the most promising candidates for the anode side exposed to reformate feedstock [9,10]. Although other bimetallic alloys, such as PtMo [11–13] and PtSn [14,15], have shown even better CO tolerance than PtRu alloys their CO_2 tolerance is worse [1,5,8]. Russell et al. [1] have shown that the lower CO_2 tolerance of PtMo compared to PtRu is owing to the difference in the mechanisms of improved CO tolerance compared to a Pt/C reference catalyst. At PtRu the mechanism is because of the water activation which occurs at Ru sites, while at PtMo the mechanism relies on the turn-over of the Mo (IV/VI) redox couple.

Many investigations have been done to develop CO tolerant binary or ternary catalysts by adding elements such as W, Mo, Co, Ni, Sn, Ir, Pd etc. to Pt/C or PtRu/C [9,16–23]. The component

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