Full Length Article

Cations promoting synthesis of self-supported nanoporous silver electrode and its catalytic activity for oxygen reduction reaction

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A R T I C L E   I N F O

A B S T R A C T

Self-supported nanoporous metals are promising catalysts and battery materials due to their continuous channels, excellent conductivity and high surface area. In this work, we found that Cu^{2+} cations could promote the spontaneous formation of AgCl on Ag surface via microcell reactions. Applying a potential to the silver electrode promotes the surface enrichment of Cu^{2+} cations, and further speeds the formation of AgCl. After electro-reduced, AgCl was transformed to self-supported silver electrode with nanoporous structures, which shows good catalytic activity for the oxygen reduction reaction and electrochemical stability together with superior methanol tolerance property, compared to the pristine silver electrode. The approach used in this work provides an alternative way to prepare self-supported nanoporous metals.

1. Introduction

Nanoporous metals are of great advantages as electrocatalysts due to the abundant porous structure, high surface area and excellent conductivity. The commonly adopted approaches to prepare self-supported nanoporous metals include dealloying process, template approach and so on. These processes are usually complex and environmentally unfriendly, so developing simple, green and economically viable process to prepare nanoporous metals is of great significance [1–10]. Silver, compared to platinum and palladium, is cheap and abundant, which is active to some reactions, i.e., oxygen reduction reaction (ORR) [11–16], carbon dioxide electro-reduction [17,18] and hydrogenation [19,20], etc. Meanwhile, Ag nanoparticles [21,22], Ag nanowires [23–25], Ag-Cu composites [26,27] and Ag-based catalysts [28–33] had been reported for electrocatalysts of ORR. In our previous work [12], we reported an electrochemical approach to prepare self-supported nanoporous silver. Simply, silver was first electro-oxidized to AgCl and then electro-reduced. By controlling the removal of Cl^- from AgCl, a self-supported nanoporous silver could be obtained. Such a top-down approach provides a way to prepare self-supporting metal electrodes, which is against the traditional electrodes Ag nanoparticle with binders, provides a large electrochemical surface area due to the binder-free structure. The electrochemical approach is simple, green, scalable and atomically economic, however, is a higher electric energy-consumption process.

In this work, we aim at exploring an approach to spontaneous formation of AgCl without or with less consumption of electric energy to produce nanoporous silver. Although in solution the reaction kinetics of Ag^+ with Cl^- to form AgCl is very fast, the products are usually irregular particles and unable to form self-supported electrode. For silver metal, once AgCl is formed on surface, the compact AgCl layer would hinder the spontaneous reaction occurring. To drive the reaction, extra energy is required. In this work, we investigate the influence of cations (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) in NaCl solution on silver surface, and found that Cu^{2+} ions is able to promote the spontaneous formation of AgCl on silver surface via microcell reactions. The spontaneously formed AgCl was then electro-reduced to form self-supported nanoporous silver. When applied just a little potential bias, which is far away from the Ag/Ag^+ potential, to the silver electrode, the formation of AgCl could be facilitated. The promotion mechanism of the AgCl formation in presence of Cu^{2+} ions is deduced. The catalytic activity, electrochemical stability and methanol tolerance ability of the obtained nanoporous silver are investigated.

2. Experimental section

2.1. Materials

All chemicals, including NaCl, $FeCl_2$, $Co(NO_3)_2$, $NiCl_2$, $CuCl_2$, NaOH, methanol, absolute ethanol, are analytically pure and purchased from Sinopharm Group. The commercial 20 wt.% Pt/C catalyst is purchased from Johnson Matthey. The deionized (DI) water (18.25 MΩ cm)
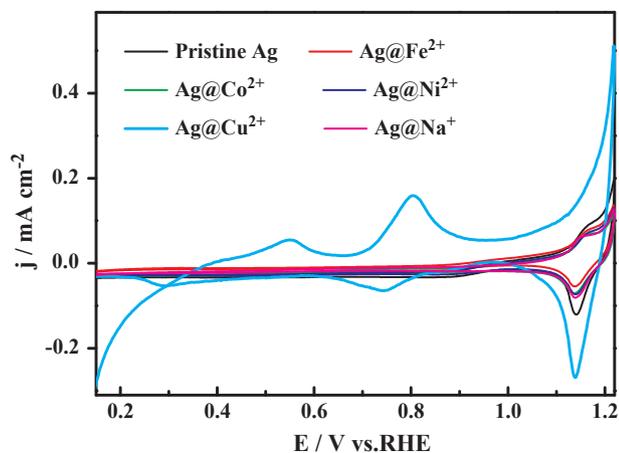
Fig. 1. CV curves of the pristine Ag disk and Ag@Me^{2+} electrodes in nitrogen-saturated 0.1 M NaOH solution. Scan rate: 10 mV s^{-1}.

were produced by UlUPure water system (UPR-II-10 T, Sichuan ULUpure Tech.). The rotating disk silver electrode (Ø 5 mm) wrapped with a PTFE coat was purchased from Tianjin Aida Company.

2.2. Electrochemical measurements

The electrochemical measurements were carried out in a traditional three-electrode system, in which the rotating silver disk was used as the working electrode. Pt wire and Hg/HgO electrode immersed in 0.1 M NaOH solution are used as the counter and reference electrode, respectively. The potentiostat adopted is CHI760E. All potentials in this paper are converted to versus reversible hydrogen electrode (RHE).

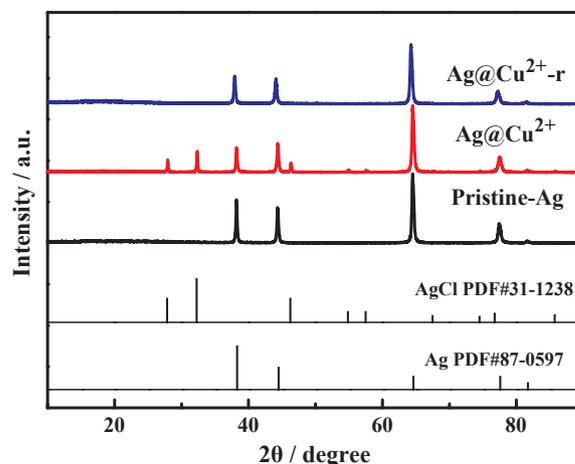The ORR polarization curves and the electrochemical stability

Fig. 3. XRD patterns of the Ag electrodes in the process of spontaneous formation of nanoporous silver.

measurements were carried out in oxygen-saturated 0.1 M NaOH and the methanol tolerance tests in oxygen-saturated 0.1 M NaOH + 1 M methanol solution. The scan rate is 10 mV s^{-1}.

2.3. Preparation of nanoporous silver

(i) *Pre-treatment of silver electrode*: before each experiment, the silver disk electrode was polished with the alumina powder (30–50 nm) to mirror, then washed with ethanol and DI water. The polished silver electrode was then electrochemically cleaned in 0.1 M NaOH solution by scanning from 0.12 to 1.32 V till a stable cyclic voltammetry curve was obtained.

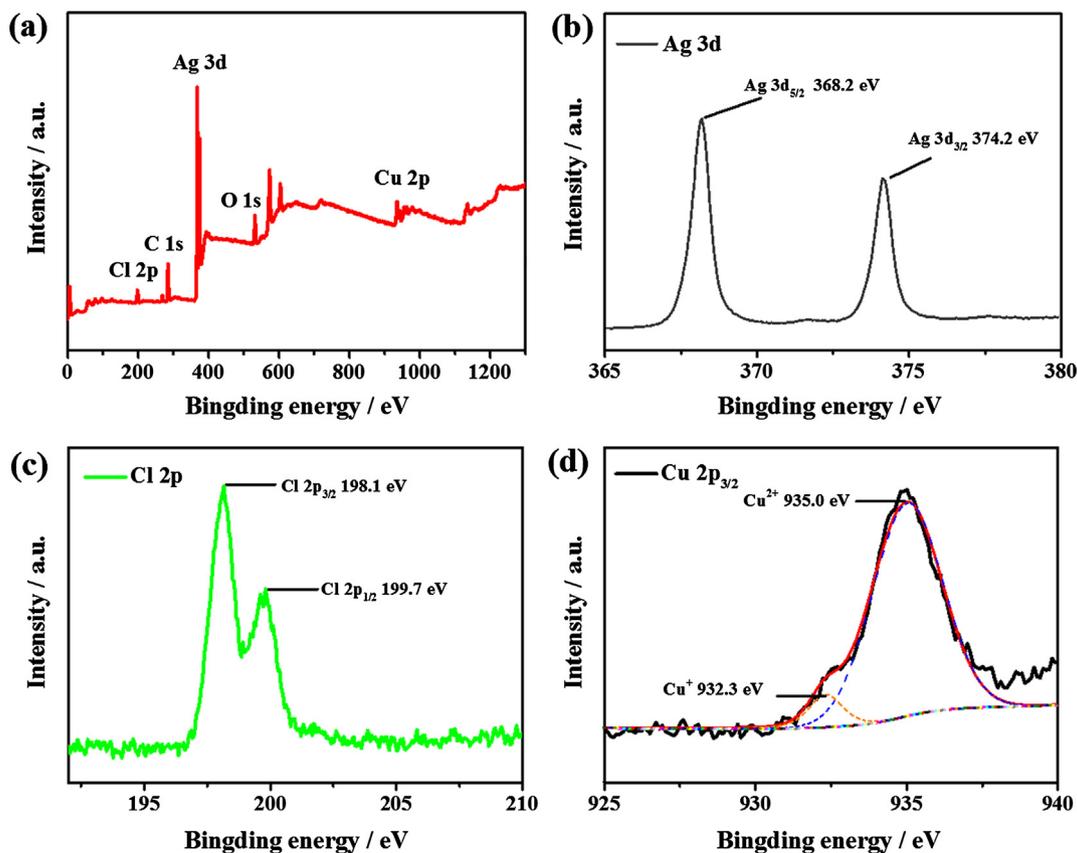(ii) *Preparation of nanoporous silver electrode via spontaneous formation*

Fig. 2. XPS survey spectra of Ag@Cu^{2+} (a) and the high-resolution XPS spectra of Ag 3d (b), Cl 2p (c) and Cu2p$_{3/2}$ (d).