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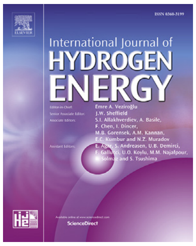

CVD grown graphene as catalyst for acid electrolytes

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ABSTRACT

Chemical Vapor Deposition (CVD) process is utilized to grow and study behavior of porous, continuous-phase 3D graphene structures in acid electrolyte. Graphene layers that are produced by CVD process are tested for oxygen reduction reaction (ORR) activity by Rotating Disc Electrode (RDE) measurements in 0,1 M $HClO_4$ electrolyte. Raman spectroscopy measurements confirms multi-layer porous structure formation for more than 1 min grow on nickel foam. Multi-layer porous graphene has provided μA level current. When NH_3 is used for nitrogen (N)-doping, magnitude of the reduction current increases, but still low for practical usage of graphene in acid electrolytes as catalyst. N-doping is confirmed with XPS measurements showing all possible types of N-doping phases with 900 °C being better than 1000 °C doping. CVD grown continuous-phase graphene, by itself or N-doped, cannot provide enough electrocatalytic activity to be used in 0,1 M $HClO_4$ acid electrolyte or polymer electrolyte membrane (PEM) fuel cells for practical applications. Pt layer of 10 nm has been sputtered on to graphene (21.45 $\mu g/cm^2$ Pt loading) and has provided orders of magnitude increase in oxygen reduction current compare to bare graphene layers.

Introduction

Polymer electrolyte membrane fuel cells are potential users in need of stable and low cost catalyst. Oxygen reduction in the PEM fuel cell cathode is the largest contributor of polarization losses and efforts continuing for improved kinetics through material innovation. Platinum (Pt) is considered as the best catalyst for oxygen reduction reaction and commonly used [1–5]. Efforts continue to replace or reduce amount of Pt with nonmetallic catalyst or non-precious metals/alloys to enhance commercial viability of electrochemical processes [6–9].

Graphite is one of the most used electrode support for its inertness as well as excellent electrical and thermal properties [10]. Graphene is the single layer of graphite providing unique features due to isotropic properties at both in-plane and through-plane structure (Fig. 1a). Each layer of spacing is 3.354 Å (A) and difficult to separate layers from each other. When several layers of graphene comes on top of each other, properties become anisotropic and 2–3 orders of magnitude of differences measured in properties between basal (in-plane) and layered (through-plane) planes. Anisotropy is resulted from multi-layer structure with graphite still carrying basic characteristics of graphene (Fig. 1b). Raman spectroscopy response with G/2D response larger than 1 indicates that multi-layer structure (Fig. 1c) leading to material called graphite.

Graphene has been researched for electro-catalytic purposes and commonly processed with chemical approaches

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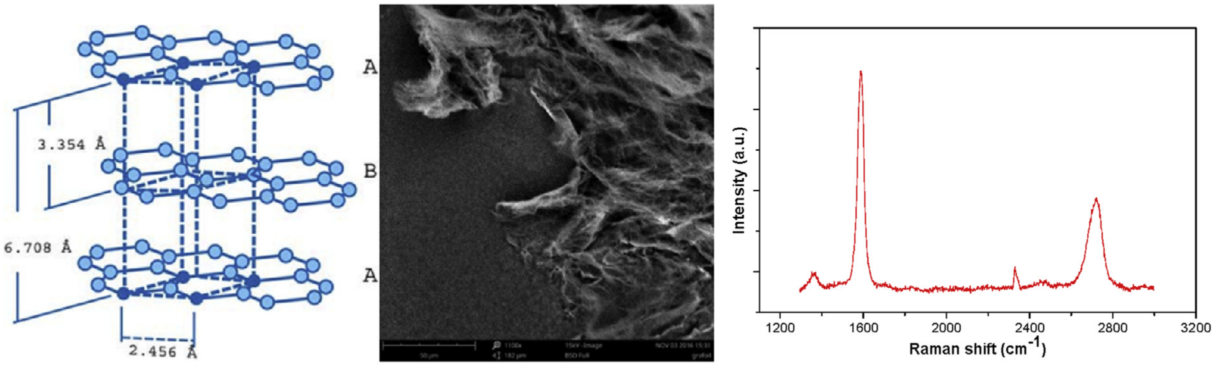

(a) (b) (c)

Fig. 1 – **Schematic layer spacing (a), SEM image (b) and Raman spectroscopy (c) for natural graphite.**

through layer separation from graphite powder. CVD grown graphene has limited studies in acid electrolytes due to processing difficulties to modify structure. Graphene produced by CVD process requires alternative processing approaches to obtain suitable materials for heterogeneous nature of gas-liquid catalytic activities. Many metals have been tried to grow graphene in CVD process, however, copper and nickel are the most used ones [11–15]. Electrocatalyst that are used in heterogeneous electrochemical systems, i.e. fuel cells, require 3-phase contact where catalyst and electrolytes homogenously distributed for charge transfer and proton exchange with gas and liquid present. If graphene can be produced in 3D form, it will help achieving fast charge transfer and high gas/liquid permeability leading to high catalyst conversion. This requires 2D foils to be replaced with 3D foams to grow graphene to take the shape of base materials [16–18]. Nitrogen (N) doping on graphene can form different defect and electronic structures for electrochemical functionality. It is shown Graphitic and Pyridinic N-doping can provide additional oxygen reduction functionality [19]. N-doping was achieved by different methods and reviewed by Rao et al. [20], and Wang et al. [21]. Most of the N-doping in the literature takes place with nitrogen precursors mixed with graphene chemically, but ammonia is also used doping agents for graphene [22–26].

Wong et al., has reviewed status of nitrogen doped carbon structures as electrocatalyst for fuel cell applications [27]. Various carbon structures with and without metal catalyst were reviewed for their performance in both acid and alkali electrolyte. Ratso et al., studied nitrogen doped graphene and carbon nanotubes for oxygen reduction in alkali electrolyte [28]. They have shown doping graphene can significantly improve oxygen reduction kinetics without metal catalyst. Kim et al., used microwave synthesis approach to co-dope graphene with boron and nitrogen and showed acceptable oxygen reduction activity in KOH [29]. Dai et al., utilized CVD

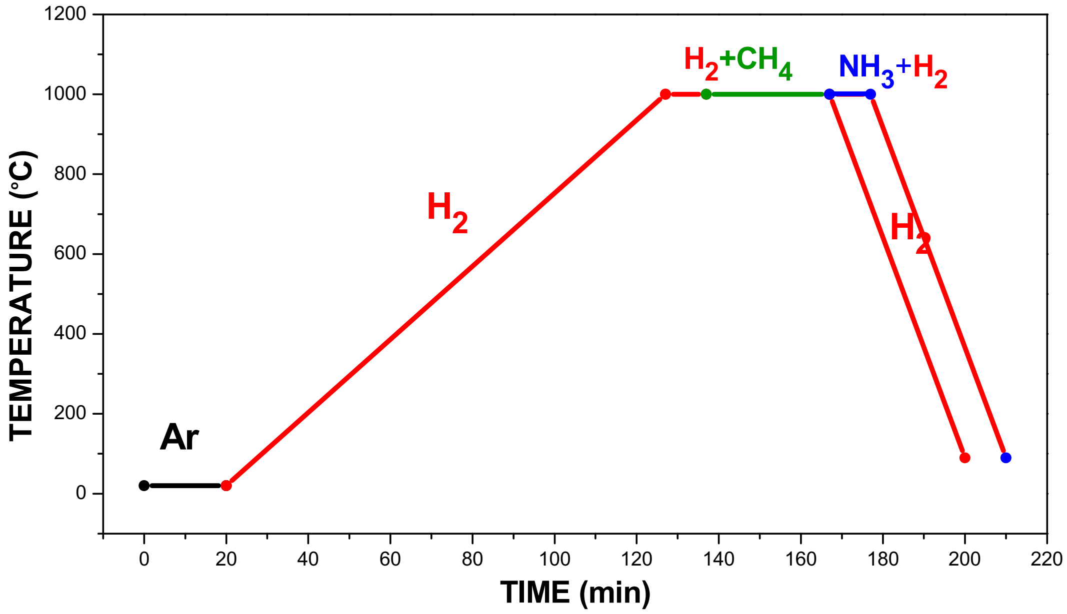

Fig. 2 – **Typical temperature-time schedule for graphene growth.**

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