Journal of Energy Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Polyaniline-based electrocatalysts through emulsion polymerization: Electrochemical and electrocatalytic performances

Q1 Shehnaz[a], Xuedan Song[a], Suzhen Ren[a,1,*], Ying Yang[a], Yanan Guo[a], Hongyu Jing[a], Qing Mao[b], Ce Hao[a,*]

Q2 [a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, Liaoning, China
[b] College of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

ARTICLE INFO

Article history:
Received 15 July 2016
Revised 23 September 2016
Accepted 28 September 2016
Available online xxx

Keywords:
Emulsion polymerization
Interfacial conductivity
Fe–Co–PANI
Non-precious metal electrocatalyst
Oxygen reduction reaction

ABSTRACT

One of the major challenges associated with fuel cells is the design of highly efficient electrocatalysts to reduce the high overpotential of the oxygen reduction reaction (ORR). Here we report Polyaniline (PANI) based micro/nanomaterials with or without transition metals, prepared by the emulsion polymerization and subsequent heat treatment. PANI microspheres with the diameter of about 0.7 μm have been prepared in basic (NH_3 solution) condition, using two different types of surfactant (CTAB, SDS) as the stabilizer, ammonium persulphate (APS) as oxidant with aniline/surfactants molar ratio at 1/1 under the hydrothermal treatment. PANI nanorods, Fe–PANI, and Fe–Co–PANI have been synthesized in acidic (HCl) medium with aniline/surfactants molar ratio at 1/2 and polymerization carried out without stirring for 24 h. Products mainly Fe–Co–PANI has shown high current density with increasing sweep rate and excellent specific capacitance 1753 F/g at the scan rate of 1 mV/s. Additionally, it has shown high thermal stability by thermogravimetric analysis (TGA). Fe–PANI has been investigated for excellent performance toward ORR with four electron selectivity in the basic electrolyte. The PANI-based catalysts from emulsion polymerization demonstrate that the method is valuable for making non-precious metal heterogeneous electrocatalysts for ORR or energy storage and conversion technology.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are a kind of promising devices with high efficiency energy conversion technology suitable for mobile and stationary applications. Two of the major issues still needing to be addressed for large-scale adoption are the cost and durability. The major contributing factor to these issues is the electrocatalyst needed for the cathodic oxygen reduction reaction (ORR). Pt has been shown to be the best monometallic catalyst material for ORR with high activity and relatively good stability in the acidic environment of the PEMFC. However, there is still a need for a more active, more stable, and less expensive cathode electrocatalysts in alkaline electrolyte to meet the demanding cost and lifetime requirements, especially for automotive propulsion power [1–3].

Non-precious metal (NPM) catalysts eliminate Pt-based electrocatalysts completely to reduce costs, and have recently shown dramatic ORR activity improvements. This advancement is achieved by carbon material and nitrogen doped carbon materials with or without transition metals, and by synthesizing the low cost electronically conductive polymers modified with non-precious metal [4–7]. Among the many approaches to prepare the NPM catalysts being explored, pyrolysis of cobalt- and iron-containing heteroatom polymer precursors (for example, porphyrins) has been the dominant route towards NPM catalysts [8–10]. The Dodelet group's impregnation and pyrolysis process combining Fe precursors and a nitrogen precursor has led to the largest beginning-of-life activity increases. However, there are still issues to be address for further advancement. One is that the nature of the active site in these NPM catalysts is still debated, as is the question of whether Fe is associated with the active site or with the means of creating such a site. The other key issues for NPM catalysts are mass transport losses and stability [11]. A polyaniline derived FeCo–C catalyst with relatively high durability (700 h) at 0.4 V in a H_2–air fuel cell and a peak power density of 0.55 W/cm^2 at 0.38 V under pressurized pure oxygen have been reported [12]. But NPM catalyst durability is worse at higher potentials and for automotive purposes, because performances at less than 0.6 V are largely irrelevant. Therefore, stability of electrocatalysts need to been improved before commercialization of the fuel cell technology.

Q3 * Corresponding authors.
E-mail addresses: rensz@dlut.edu.cn (S. Ren), haoce@dlut.edu.cn (C. Hao).
[1] Fax: +86 411 84986492.

http://dx.doi.org/10.1016/j.jechem.2016.11.013
2095-4956/

Nanostructured electronically conductive polymers have gained attention in recent years. Due to its enormous properties in sensors, field emission, light emitting diodes and capacitors, it became one of most studied research topic in literatures [13,14]. Choosing nitrogen containing compound having aromatic carbon rings, PANI is the best candidate for nanostructured conductive polymer, having excellent electrochemical and ORR activity dependent on its morphology [15]. PANI applications are based on its vast morphology such as nanorods, nanotubes, nanofibers, nanowires and nanospheres, dependent on its synthetic method [16]. Cheng et al. have explained control synthesis of PANI nanofibers and nanotubes and described its applications in lithium rechargeable batteries [17]. Mutyala et al. have demonstrated the synthesis and electrochemical activity of nitrogen doped PANI toward ascorbic acid electro-oxidation [18]. Feng et al. have described the synthesis of Nitrogen-doped carbon nanotubes/polyaniline composites, used as electrode materials for biosensors and showed its high catalytic activity for oxidation of dopamine in a neutral environment [19]. Zhou et al. have synthesized PANI nanofibers with high electrical conductivity from CTAB-SDBS mixed surfactant [20]. Bagdanovic et al. have prepared Au–PANI nanocomposite with high conductivity (1.19 S/cm) and excellent electrocatalytic activity toward electrochemical O_2 reduction through interfacial polymerization [21]. Silva et al. have prepared polyaniline-microspheres through electrochemical synthesis in the presence of iron sufate and citric acid and described that iron oxide in polymeric matrix decreased the thermal properties of the materials [22]. While describing the synthetic route for synthesis of PANI nanostructure, chemical and electrochemical polymerization of monomer with aid of either soft template or hard template method has been used. Qiu et al. have synthesized highly ordered polyaniline-nanorods by oxidative polymerization in presence of sucrose stearate surfactant acting as a soft template and acetone as solvent, demonstrated that concentration of sucrose stearate exhibited a strong influence on nanorods diameter [23]. Soft template method includes emulsion [24,25], micro-emulsion [26,27], diffusion polymerization [28], and interfacial polymerization which can be regarded as an efficient method for preparing PANI nanostructure [29].

Emulsion polymerization is the most common process for production of dispersed polymers, also called latexes [30]. This process requires the use of amphiphilic molecule or surfactant that have great importance in production and application of dispersed polymers. Surfactants play an important role in nucleation of latex particle, emulsification of monomer droplets and/or preformed polymer, stabilization of polymer particles during polymerization and self-life of products. Surfactant-assisted polymerization of aniline provides improved colloidal solubility, conductivity, stability, processibility, and supramolecular structure of conducting polymer. Mixed surfactant (cationic, anionic) concentration and reaction medium (acidic, basic) are two important factors for the formation of well controlled morphology of polyaniline. Spherical morphology dominates in low surfactant concentration (in basic media) while high surfactant concentration (in acidic media) leads to nanorods formation. When concentration of surfactant is low in an aqueous solution, the surfactants are located as separate molecules in air/water interface. This reduces the surface tension since it is larger for water than for hydrocarbons. Increasing the surfactant concentration in solution further reduces the surface energy until a critical value. At this point, the critical micelle concentration (CMC) is reached and aggregates of surfactant (micelle) are formed which leads to formation of nanorods like morphology [31].

PANI–metal has been investigated due to its excellent applications both for electrochemical as well as for electrocatalytic activity but its synthesis is one of crucial step due to its insolubility in any solvent. Our main motivations are (i) to develop suitable environmental friendly synthetic route for synthesis of PANI–metal (metal must be non-precious = Fe, Co); (ii) synthesis of PANI-based materials of different morphologies with excellent electrochemical and electrocatalytical activities.

Here in, we reported the morphology control synthesis of PANI and PANI–metal electrocatalysts in the presence of mixed surfactant, metal salt under acidic and basic media (nanorods and microspheres), determined their enhanced electrochemical properties and ORR activity for PEMFC. Our results demonstrate that the Fe–Co–PANI exhibits high capacitive performance of 1753 F/g at scan rate 1 mV/s as compared to Fe–PANI, PANI microspheres and nanorods. Furthermore, Fe–Co–PANI presents a good cycling stability with 89% of capacity retention after 1000 cycles, much higher than PANI microspheres (60%).

2. Experimental

2.1. Chemical reagents

The ammonia solution (25%), ethanol (AR), HCl (30%), aniline, ammonium persulphate (APS), iron nitrate hexahydrate $Fe(NO_3)_2 \cdot 6H_2O$, cobalt nitrate hexahydrate $Co(NO_3)_2 \cdot 6H_2O$, Ferric chloride $FeCl_3$, Sodium dodecyl sulphate (SDS) and cetyltrimethyl ammonium bromide (CTAB) were gained from Damo Reagent, Tianjin, China. Water used in the whole experiment was doubly distilled.

2.2. Synthesis of PANI microspheres

In a typical procedure 0.5 mL aniline was added in 10 mL of 0.008 M ammonia solution. 5 mL of 0.005 M CTAB and 5 mL of 0.0042 M SDS were added into the above solution under continuous stirring and sonicated about 15 min. 5 mL of 0.007 M APS dissolved into above reaction mixture, transferred into autoclaves and put under thermal treatment at about 85 °C for 5 h in oven.

2.3. Synthesis of PANI nanorods

5 mL of 0.0084 M SDS and 5 mL of 0.01 M CTAB were added into 35 mL aqueous solution of 0.027 M HCl. 0.5 mL aniline was added after 10 min at room temperature under continuous stirring. Put into sonication for about 15 min. 10 mL of 0.02 M APS was added into above solution and left the solution for 3 h polymerization.

2.4. Synthesis of Fe–PANI nanorods

The same procedure as described for polyaniline nanorods just changed after sonication under stirring added 15 mL of 0.016 M $Fe(NO_3)_2$. 10 mL of 0.02 M APS was added after 1 h stirring and put the reaction mixture without stirring for 24 h.

2.5. Synthesis of Fe–Co–PANI nanorods

All procedure is the same as polyaniline nanorods, just changed after aniline addition and sonication under stirring, added 10 mL of 0.061 M $Co(NO_3)_2$. 10 mL of 0.0053 M $FeCl_3$ and 10 mL of 0.02 M APS were added after half an hour. Put reaction 24 h without stirring.

All PANI samples were washed with water and ethanol several times, dried at 60 °C for 8 h. 0.1 g powder of all as synthesized samples was put under nitrogen atmosphere at heat treatment of about 500 °C to produce polyaniline-based electrocatalysts.

2.6. Characterization

The morphology and structure of as-prepared PANI (microspheres, nanorods) and PANI–metal (Fe, Fe–Co) were investigated by means of scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR). SEM images were taken using a QUANTA 450 (FEI, America), which was together with Energy Dispersive Spectroscopy (EDS) to observe the chemical composition of samples. N_2 adsorption–desorption measurements were

Please cite this article as: Shehnaz et al., Polyaniline-based electrocatalysts through emulsion polymerization: Electrochemical and electrocatalytic performances, Journal of Energy Chemistry (2016), http://dx.doi.org/10.1016/j.jechem.2016.11.013