# Hydrogen production by proton exchange membrane water electrolysis using cobalt and iron hexachloroclathrochelates as efficient hydrogen-evolving electrocatalysts

CrossMark

S.A. Grigoriev [a,*], A.S. Pushkarev [a,b], I.V. Pushkareva [a,b], P. Millet [c], A.S. Belov [d], V.V. Novikov [d], I.G. Belaya [d], Y.Z. Voloshin [d,e]

[a] National Research University "Moscow Power Engineering Institute", 14, Krasnokazarmennaya St., 111250 Moscow, Russia
[b] National Research Centre "Kurchatov Institute", 1, Kurchatov Sq., 123182 Moscow, Russia
[c] Institut de Chimie Moléculaire et des Matériaux D'Orsay, Université Paris-Sud 11, 91405 Orsay, France
[d] Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28, Vavilova St., 119991 Moscow, Russia
[e] Gubkin Russian State University of Oil and Gas, 65, Leninsky Prospekt, 119991 Moscow, Russia

## ABSTRACT

Cobalt and iron(II) hexachloroclathrochelates with apical aliphatic and aromatic substituents were synthesized and characterized using cyclic voltammetry. The obtained clathrochelate-based systems were impregnated on the surface of carbon paper and tested as cathode electrocatalysts in water electrolysis cell with proton exchange membrane (PEM). Both the cyclic voltammograms and the current–voltage performances of membrane-electrode assemblies suggested that these cage complexes can be successfully implemented in PEM water electrolyzers and used as efficient electrocatalysts for hydrogen evolution.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

A great technological challenge for a global future is the search for safe, green and renewable energy sources [1,2]. Indeed, an increase in energy demand derived from economical and population growth will soon result in even higher carbon dioxide emissions. The impact on climate change can have dramatic consequences for humanity. Hydrogen is a potential alternative to carboniferous fossil fuels if obtained from an appropriate source [1]. Carbon intensity will be decreased significantly if water is the primary

---

carbon-neutral $H_2$ source. On the other hand, the wide use of various electrochemical systems (fuel cells, water electrolyzers, etc.) in modern hydrogen energy [3], high technology industries, green hybrid and hydrogen-based transports, and other fields of modern social and economic life, may cause a substantial increase in consumption of precious metals, which are currently used as electrocatalysts for hydrogen production. Their high cost significantly limits the widespread use of such electrochemical systems in hydrogen energy. The use of cheap and abundant non-platinum $3d$-metal compounds in fuel cells, electrolyzers and electrochemical hydrogen compressors/concentrators in nuclear power is a potentially very attractive alternative solution that will make hydrogen energy more available than ever. Over the last decade, cage metal complexes, such as clathrochelates [4,5] containing an encapsulated cobalt or iron(II) ion have been intensively tested as potent non-platinum molecular catalysts or precatalysts of hydrogen evolution reaction (HER) in harsh acidic media and strongly acidic aqueous solutions [6–15]. The potentials of reduction of an encapsulated metal(II) ion in these clathrochelates, leading to the formation of metal(I) oxidation states [16,17] or even fully reduced metal-containing nanoparticles [7,18], can be decreased using strong electron-withdrawing substituents in their ribbed fragments [16], including halogen atoms in such chelate moieties [9,18]. In this communication we report the results obtained with a series of the cobalt and iron(II) hexachloroclathrochelates that used as the components of clathrochelate-based cathode electrocatalytic systems in membrane-electrode assemblies (MEAs) of PEM water electrolysis cell.

# Experimental

## Synthesis of metal(II) hexachloroclathrochelates

Cobalt and iron(II) hexachloroclathrochelates (Fig. 1) with apical aliphatic and aromatic substituents were prepared by known synthetic procedures [16,17,19,20] using direct template condensation of dichloroglyoxime with an appropriate boronic acid on the corresponding metal ion as a matrix. Due to low donor ability of the above α-dioxime, such self-assemblies were performed under vigorous reaction conditions using boiling nitromethane as a solvent with partial distillation of nitromethane − water azeotrope.

## Solution cyclic voltammetry experiments

Cyclic voltammetry experiments for cage complexes under study were carried out for their dichloromethane solutions using 0.15 M TBAP as a supporting electrolyte. Measurements were made in a conventional one-compartment three-electrode cell (5 ml of solution) using a Metrohm Autolab PGSTAT128N potentiostat. Glassy carbon disk electrode (MF-2012, BASi, 3 mm diameter), used as a working electrode, was thoroughly polished with 0.05 μm alumina slurry, sonicated for two minutes in deionized water and rinsed before every measurement. A platinum wire was used as a counter-electrode and Ag/AgCl/NaCl$_{aq}$ (RE-5B, BASi) was used as a reference electrode. The ohmic drop between the reference

and working electrodes was compensated using positive feedback circuit of the Autolab PGSTAT128N potentiostat. To account for the potential drift of the reference electrode during the experiments, ferrocene (Fc) was added after the measurements as an internal standard, and all the potentials are reported relative to the Fc/Fc$^+$ redox couple. The solutions were thoroughly deaerated by bubbling argon before the cyclic voltammetry experiments and during the measurements, an atmosphere of argon was maintained above the solutions to avoid their air contamination.

## Functionalization of gas diffusion electrodes with metal(II) clathrochelates

The obtained metal(II) hexachloroclathrochelates were impregnated on gas diffusion electrodes (GDEs) of circular shape. The corresponding GDE was immersed in a dichloromethane solution of the corresponding clathrochelate complex for 3 min followed by decantation of this solution and drying of the obtained clathrochelate-modified GDE in air. Sheets of Sigracet® 10BB carbon paper with microporous sublayer (SGL CARBON GmbH, Germany) of 7-cm² surface area, thickness of $ca.$ 0.4 mm and porosity of 84% were used as GDEs. The estimated loading of clathrochelate-based catalyst is $ca.$ 5–12·$10^{-4}$ mg·cm$^{-2}$ for all the samples.

## Fabrication and tests of the membrane-electrode assemblies

Clathrochelate-impregnated GDEs were studied as cathodes of MEAs in PEM water electrolysis cell. Nafion® 117 membrane (DuPont, USA) was used as a solid polymer electrolyte in the above MEAs. A MEA containing the conventional carbon-supported platinum electrocatalyst [21–24] at the cathode was prepared and used as reference to compare the performance levels. Pt nanoparticles (Pt loading of $\approx$ 40 wt.%) were deposited onto Vulcan XC-72 using magnetron-ion sputtering method [24–26]. Ir black, obtained by chemical reduction of the solvato-complex $H_2IrCl_6·6H_2O$ with $NaBH_4$ as an reductant [21,22], was used as an anode electrocatalyst of oxygen evolution reaction (OER) in all these MEAs. All MEAs have circular configuration with a diameter of 3 cm and a surface area of $ca.$ 7 cm². Both the anodic and cathodic catalytic layers were prepared by spraying Ir and XC-72-supported Pt catalyst over the surface of the GDEs. The catalyst and 5 wt.% Nafion® solution (Du Pont) were homogenized in $iso$-propanol using an ultrasonic bath with the working frequency of 22–25 kHz for 20 min. The ionomer content of the mixture on a dry basis was 5 wt.% for Ir black and 15 wt.% for Pt/Vulcan XC-72. The resulting catalytic ink was sprayed onto GDEs with an intermittent dryings of the deposited layers. Loadings of Ir and Pt/Vulcan XC-72 catalysts were approximately 2 and 1 mg·cm$^{-2}$, respectively. Porous titanium disks (7-cm² surface area, 0.9-mm thickness and 30%-porosity) were used as anodic GDEs. Sigracet® 10BB carbon paper was used as GDE in the case of Pt/Vulcan XC-72 as well as in the case of metal(II) cage complexes under study. After preparation, the MEAs were tested in a lab-made titanium electrolysis cell consisting of two thermostatic half-cell with the MEA clamped in between [24]. The cell temperature was set to 80 °C, and liquid water was pumped continuously through the anode compartment.