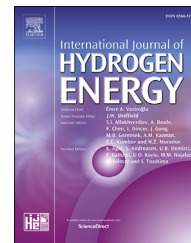


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A newly synthesized single crystal zinc complex as molecular electrocatalyst for efficient hydrogen generation from neutral aqueous solutions

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ABSTRACT

A new chlorobis(2-aminomethylbenzimidazole)zinc(II) perchlorate complex [Zn(AMB)₂Cl](ClO₄) **1** has been synthesized and characterized. Spectral and X-ray structural features led to the conclusion that the zinc(II) complex has a square-pyramidal environment around zinc(II) center with coordination chromophore ZnN₄Cl. Different amounts of complex **1** were supported on glassy carbon (GC) electrode yielding three GC-supported complex **1** electrodes with different loading densities (0.2, 0.4, and 0.8 mg cm⁻²). These electrodes were tested as molecular electrocatalysts for the hydrogen evolution reaction (HER) in phosphate buffer aqueous solutions (pH 7), employing linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Results showed that GC-complex **1** catalysts are highly active for the HER, and this catalytic activity enhances with the loading density. The one with the highest loading density (0.8 mg cm⁻²) exhibited high HER catalytic activity with low onset potential of -140 mV vs. RHE and a high exchange current density of 0.22 mA cm⁻². It required an overpotential of 240 mV to achieve a current density of 10 mA cm⁻². It also recorded a turnover frequency (TOF) of 1722 mol of hydrogen per mole of catalyst per hour at overpotential 500 mV, which is comparable with the most active molecular electrocatalysts reported in the literature for H₂ generation from aqueous neutral solutions. A catalytic cycle is proposed for the generation of hydrogen by complex **1** and the mechanism of the HER is discussed based on the measured Tafel slope (140 mV dec⁻¹).

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Introduction

Hydrogen (H₂) gas, a versatile energy carrier with favourable characteristics, and a high-energy-density fuel [1–3], production has become essential due to enhanced global energy demand [4]. Steam reforming of the natural gas is the most economical and dominant technology for direct generation of hydrogen, since natural gas is abundant, non-precious, and include the highest content of H₂ among all fossil fuels [5]. However, this industrial process requires high energy and emits CO₂ gas as a by-product, which causes global warming and contributes increasing the natural acidity of rainwater (acid rains) [6–8]. Therefore, it is essential and highly desirable to develop safe (environmental friendly) and efficient approaches to generate H₂ from sources other than fossil fuels.

Water electrolysis is an alternative, most economical and promising technology for sustainable greenhouse – H₂ free production [1–3]. Hydrogen evolution reaction (HER), the reductive half-reaction of water splitting, is one of the most studied electrochemical reactions, but still remain technical challenge, since it controls the efficiency of energy conversion devices [9]. Platinum (Pt) and Pt-based materials are well known as the most efficient catalysts capable of catalyzing the HER [10–13]. However, the low abundance and high cost of these materials limit their widespread applications [14].

Various attempts have been, and being made to replace the expensive Pt and Pt-based materials by a stable, highly efficient, non-precious, and earth-abundant catalysts for the HER [9,15]. Most of these cheap effective catalysts are based on earth-abundant metals [9,15–28]. Also, carbon-based, metallic [29] and non-metallic [30], and metal-supported metallic nanoparticles [31–33] materials proved to be superior, inexpensive electrocatalysts for the HER.

Molecular electrocatalysts, e.g., transition-metal complexes, are another class of materials that can also play an important role in energy storage and conversion devices [34]. They are highly stable materials and considered as excellent means for energy storage in chemical bonds and electricity generation via hydrogen production and oxidation, respectively [35]. It is a real challenge for coordination chemists to fabricate and develop transition metal complexes capable of catalyzing the reduction of protons (H⁺) to H₂ at low overpotentials [36]. In this context, the first row transition metal-based complexes have been reported as efficient molecular electrocatalysts for the HER [37–40]. However, and to the best of our knowledge, most of these metal-complex electrocatalysts were tested in non-aqueous solutions. Literature revealed very limited publications on electrochemical hydrogen generation on metal-complex electrocatalysts in aqueous solutions [41,42]. Here we synthesized a new single crystal metal complex, namely chlorobis(2-aminomethylbenzimidazole)zinc(II) perchlorate complex which can be used to modify electrodes with the objective to produce cathodes with high catalytic activity for the HER from water. Various electrochemical techniques were employed here to assess HER activity of the studied GC-complex 1 catalysts. Stability and long-term durability of the best catalyst were also evaluated using cyclic voltammetry (repetitive cycling up to 5000 cycles) and chronoamperometry measurements.

Experimental

Materials and instrumentations

Caution! Perchlorate salts being potentially explosive, only small quantity was handled with care. All chemicals used were of analytical grade, purchased from Sigma. The zinc(II) perchlorate hexahydrate salt and the ligand 2-aminomethylbenzimidazole dihydrochloride were obtained from Aldrich. Infrared spectral measurements for the free ligand and its zinc complex were recorded using Alpha-Attenuated FT-IR Spectrophotometer, Bruker in the range of 400–4000 cm⁻¹. ¹H NMR spectra of the ligand and its zinc complex were recorded using Varian 400-NMR spectrophotometer employing TMS as a reference and DMSO-*d*₆ as a solvent at ambient temperature. The specific conductance of the complex was measured using freshly prepared (10⁻³ M) solutions in water at ambient temperature, using YSI Model 32 conductance meter.

Synthesis of zinc(II) complex [Zn(AMB)₂Cl]ClO₄

A solution of Zn(ClO₄)₂·6H₂O (0.372 g, 1.0 mmol) and the ligand 2-(aminomethyl)benzimidazole dihydrochloride (AMB·2HCl) (0.44 g, 2.0 mmol) treated with NaOH (0.08 g, 2 mmol) in methanol (30 mL) was refluxed for 2.0 h. The resulting solution was stirred for another 2 h at room temperature and then the solution was concentrated to 10 mL. Colorless crystals were obtained after three days. Filter, and dried in vacuum. Analytical calculated for C₁₆H₁₈Cl₂N₆O₄Zn (494.64): C, 38.85; H, 3.67; N, 16.99; Cl, 14.33; Zn, 13.22%. Found: C, 39.35; H, 3.88; N, 16.85; Cl, 14.02; Zn, 13.37%. ¹H NMR (400 MHz; CD₃OD:D₂O): 4.25 (4H, s, –CH₂–), 7.27, (4H, H_b) and 7.45 (4H, H_a). IR: ν (cm⁻¹): 3326 [ν_{st}(N–H)], 3260 [ν_{st}(C–H)], 1624 [ν_{st}(C=N)], 1455 [σ(N–H)], 1064 [ν(ClO₄)], 621 [ν_{st}(–NH₂)].

X-ray single-crystal determination of zinc(II) complex [Zn(AMB)₂Cl]ClO₄ 1

Crystallographic data of zinc(II) complex (Table 1) were collected on a Smart CCD diffractometer of Bruker AXS using Mo-Kα radiation. The crystal does not show significant intensity loss through data collection (Table 2). Lorentz-Polarization corrections were performed by SAINT [43]. Absorption corrections were made by using SADABS [44]. The structures were solved by direct or Patterson methods using SHELXS-2013 [45] to find the position of heavy atoms. Other non-hydrogen atoms were located by Fourier syntheses and refined using SHELXS-2013 [45].

Electrochemical measurements

Materials and solutions

All solutions were analytical grade chemical reagents (Sigma-Aldrich), and freshly prepared using water purified by a Millipore Milli-Q system (resistivity: 18.2 MΩ cm). A homogeneous, well-dispersed electrocatalyst ink was first prepared by dispersing 4 mg of complex 1 in a mixture of deionized water and ethanol in a 4:1 ratio (v/v). 80 mL Nafion was then added to

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