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Oxygen reduction catalyzed by a Carbohydrazone based compound at liquid/liquid interfaces

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ABSTRACT

Ferrocen, (Fc), can reduce oxygen to water or hydrogen peroxide at a water/1,2-dichloroethane (DCE) interface which proceeds as a proton coupled electron transfer process. In this work, the oxygen reduction reaction (ORR) by Fc has been investigated in the presence of bis-[(*E-N′*-(phenyl(pyridin-2-yl)methylene)]carbohydrazide (H_2L) that acts as proton ionophore for transferring of protons from the aqueous phase to the organic phase. H_2L shows two peaks at low pH (less than pH = 3.5) and one peak at pH = 3.5. The two waves of H_2L shift to negative potentials with increasing the acidity of aqueous phase. It can be said that both waves correspond to a facilitated proton transfer reaction.

1. Introduction

The oxygen reduction reaction (ORR) is very important process in energy converting systems like metal-air batteries, fuel cells, corrosion and in life processes such as biological respiration [1–3]. Electrochemistry at the liquid/liquid interface, which so-called interface between two immiscible electrolyte solutions (ITIES), provides a well reproducible platform to study proton-coupled electron transfer (PCET) reactions. In PCET reactions protons locate in the aqueous phase and electron donors locate in the organic phase, respectively [4–6]. ITIES has recently attracted much interest for energy and environmental research, such as ORR, [7–9]hydrogen generation [10,11]and carbon dioxide reduction [12]. ORR at the ITIES has been studied by using various organic electron donors, decamethylferrocene (DMFc), [13,14] flavin mononucleotide (FMN), [15] tetrachlorohydroquinone (CQH_2), [16] and fullerene monoanion [17]. So far, various ionophores such as dodecylaniline [14], 3,5,N,N-Tetramethylaniline, N,N-Diethylaniline, 4-Nitroaniline, 4-Dodecylaniline [18], 5,10,15,20-tetraphenylporphyrin [19] and fluorinated tetraphenylporphyrin free base [6] have been used as catalyst for oxygen reduction at ITIES. Ionophores such as 4-DA can facilitate proton transfer from the aqueous to the organic phase [14]. Some ligands like amine derivatives, free base porphyrin and Schiff base ligands can act as proton ionophore in the ORR, too.

The reaction between aldehyde/ketones and primary diamines produces Schiff base compounds [20,21]. Schiff base complexes have been widely used in the reactions such as epoxidation [22], asymmetric synthesis [23], asymmetric sulfoxidation [24], asymmetric silylcyanation [25]and many other applications [26].Hydrazones are a special group of organic compounds in the Schiff base family which are characterized by the presence of the RRT′C═N—NH—C(═O)R″ moiety. Due to the availability of several potential donor sites and facile keto-enol tautomerization, hydrazones represent versatile chelating ability with interesting coordination modes [27–30]. Carbohydrazones are special type of symmetric dihydrazones (Scheme 1) which have several nitrogen atoms and show high stability in acidic and basic media. In the acidic media they can attract hydrogen atoms to form cationic moiety via several nitrogen atoms and the anion can stabilize in the crystal packing by hydrogen bonding interactions [31]. This behavior is seen in other hydrazone based Schiff bases, too [32,33]. Moreover, due to facile keto-enol tautomerization, they can lose the hydrogen atom of —N-H—C(═O)— group to form a mono-negative organic anion and show acidic behavior. Such behavior is frequently seen in the coordination of carbohydrazones to the metal ions [34–37]. Therefore, these compounds have high stability and versatility in acidic or basic media which makes them strong and efficient reagents for proton transferring processes. Nevertheless, there are not considerable studies on the applications of this behavior of carbohydrazone compounds.

By considering the applications of organic compounds in ORR systems and also the high potential of carbohydrazone based compounds in transferring proton (hydrogen atom), we interested to employing carbohydrazone based compound as proton ionophore for transferring of protons from the aqueous phase to the organic phase in ORR system. We have recently reported our study on the catalytic effects of cobalt-carbohydrazone complex on the molecular oxygen reduction at the liquid/liquid Interface [38]. In the present work, the catalytic effects of the free carbohydrazone Schiff base compound (H_2L)

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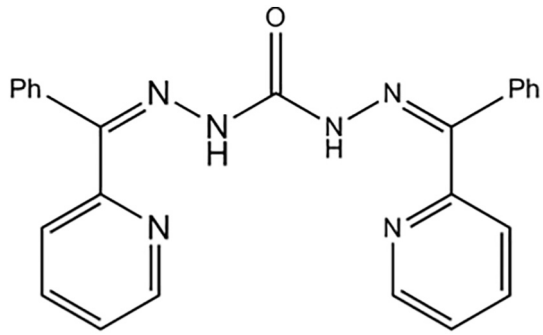
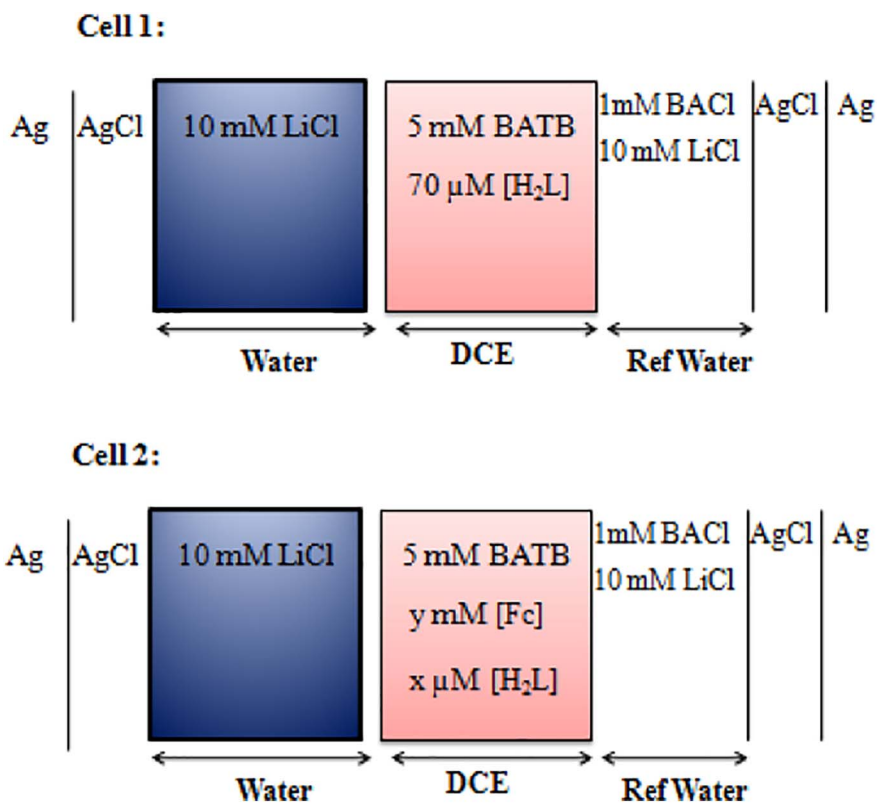


Scheme 1. Structure of bis-[(*E*)-*N′*-(phenyl(pyridin-2-yl)methylene)]carbohydrazide (H_2L).

chemicals were used as received without further purification. Bis (triphenylphosphoranylidine) ammonium tetrakis(pentafluorophenyl) borate (BATB) was prepared by a metathesis of 1:1 mixture of BACl and LiTB in methanol/water (V:V = 2:1) followed by recrystallization from acetone. Compound bis-[(*E*)-*N′*-(phenyl(pyridin-2-yl)methylene)] carbohydrazide (H_2L) was synthesized and characterized according to our previous report [38,39].

2.2. Electrochemical measurements

Electrochemical measurements at the water/DCE interface were performed in a four-electrode configuration on a commercial micro-potentiostat (PGSTAT 101, Eco-Chemie). The electrochemical cell was used a three-compartment glass cell. Two platinum counter electrodes were positioned in the aqueous and DCE phases, respectively, to supply the current flow. An external potential was applied between two



Scheme 2. Composition of the electrochemical cells used in this study.

on the reduction of oxygen by Fc was investigated at water/DCE interfaces. In this case, the rate of ORR in the presence of both Fc and H_2L, (Scheme 1) is significantly higher than the only Fc in the organic phase.

2. Experimental

2.1. Chemicals reagents

Bis(triphenylphosphoranylidine) ammonium chloride (BACl 98%), lithium tetrakis(pentafluorophenyl)borate ethyl etherate (LiTB), lithium chloride (LiCl > 99%), potassium iodide (KI, 99%) and ferrocene (Fc, 98%), hydrochloric acid (37%) and 1,2-dichloroethane (DCE) were purchased from Sigma-Aldrich. Carbohydrazide and 2-benzoylpyridine were purchased from Acros and used as received. All of these

reference electrodes, silver/silver chloride (Ag/AgCl), which connected to the aqueous and DCE phases respectively by means of a Luggin capillary. Electrolyte compositions are illustrated in (Scheme 2). The potential was converted to the Galvani potential difference ($\Delta_0^{W}\Phi$), based on cyclic voltammetric measurement of the reversible half-wave potential of the TMA^+ cation transfer (0.16 V) [40]. All electrochemical measurements were performed at ambient temperature (23 ± 2 °C).

2.3. Two-phase reactions

The two-phase reactions were performed in a small flask under stirring conditions. Firstly, the DCE solution (1 mL) containing 4 mmol L^{-1} Fc and 70 μmol L^{-1} of H_2L was added to the flask, followed by the addition of 1 mL of aqueous solution containing 10 mmol L^{-1} of HCl. The salt of the common ion (TB^-), LiTB, was

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