



N-heterocyclic carbene–silver complex as a novel reference electrode in electrochemical applications

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ABSTRACT

We demonstrate a novel reference electrode material namely an organometallic silver complex e.g., silver (I) tetramethylbis(benzimidazolium) diiodide [1a] for both acid and alkaline electrolysis. The potential usage of the silver complex as a reference electrode with at least equal electrochemical capabilities compared to those of the conventional electrode materials (e.g., Hg/HgO in alkaline media and Ag/AgCl in acidic media) are also demonstrated using cyclic voltammetry. In addition, the well dispersed surface morphology and fine crystallinity of the silver complex is investigated using field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD).

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1. Introduction

Due to the great advantages of Ag/AgCl electrode systems being stable and robust in addition to the easy and cost-effective fabrication procedure, this has been the most commonly used reference electrode for various electrochemical measurements performed in acidic media. However, when using the Ag/AgCl reference electrode in alkaline media-based electrochemical measurements, it could be extracted as silver oxide complexes which could result in a large error for reference electrode potential measurements. Moreover, cell potential measurements involving dramatic changes in pH values of media could cause inaccurate and poor reproducibility in the measurements. Alternatively, Hg/HgO reference electrode systems can be powerfully utilized in alkaline solution electrochemistry, however, there are still great demands required on developing an alternative environmentally-friendly, stable and cost-effective reference electrode system for an alkaline media-based electrochemical measurements [1–3]. Thus, herein we report an effective substitution material, namely, an organosilver complex, silver (I) tetramethylbis(benzimidazolium) diiodide [1a] for the reference electrode in both alkaline and acid solution electrochemistry.

The synthesis and isolation of stable free imidazolylidene by Arduengo et al. [4] along with initial reports by Öfele [5] and Wanzlick and Schonherr [6], have spurred research on N-heterocyclic carbenes (NHCs) [7,8] which are extremely versatile ancillary ligands in organometallic chemistry. These ligands can successfully take the place of phosphines and be coordinated as multi-dentate way to uptake the transition metals [9]; thus, many of such transition metal carbene complexes have been prepared [10,11]. For example, the structures, reactivities and chemical properties of a number of azole-based transition metal complexes are known and these species are of great utility in synthetic organic chemistry [12,13], catalysis [14] and chemical materials [15–17]. For NHC–Ag complexes [18–20], due to a linear geometry of silver (I), most of these complexes are reported as mononuclear or binuclear molecules and sometimes two dimensional multinuclear oligomers depending on the structure of NHC. Specifically the bidentate bibenzimidazole-based ligands provide the main-chain organometallic polymers in case of such Pd, Pt [21,22]. For the aspect of silver, most NHC–Ag complexes have been used as catalytic materials such as transmetalation and ionic liquid crystal [23–25].

In this paper, silver (I) tetramethylbis(benzimidazolium) diiodide [1a] was first synthesized and characterized by NMR, UV/vis, emission, SEM and XRD method. The silver complex [1a] was

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then applied as a reference electrode in both acid and alkaline electrolysis.

2. Experimental

2.1. Chemicals and instrumentation

For the synthesis of silver complex, all chemicals are used without purification as received from the Aldrich chemicals otherwise specified. Solvents were purified and degassed by standard procedures. ^1H NMR (400 MHz) and ^{13}C NMR (75.46 MHz, 150.83 MHz) were recorded on a Bruker Advance Digital 400, 600 NMR spectrometer and chemical shifts were recorded in ppm units using SiMe_4 as an internal standard. Coupling constants are reported in Hz. Infrared spectra were recorded on Bruker FT/IR-Alpha (neat) and the data are reported in reciprocal centimeters. Elemental analyses and ICP (inductively coupled plasma) were performed by Fison-EA1108 and Thermo IRIS XDL duo, respectively. Absorption and emission spectra were obtained on Jasco V-530 UV/vis spectrophotometer and Jasco FP-6500 spectrofluorometer, respectively. The surface morphology and crystal structure of the prepared Ag complex electrode were analyzed using field-emission scanning electron microscopy (FE-SEM; Hitachi S-4700) and X-ray diffraction (XRD; Rigaku, D/MAX Ultima III) using $\text{Cu-K}\alpha$ radiation, respectively.

2.2. The preparation of silver (I)

tetramethylbis(benzimidazolium) diiodide [1a]

Tetramethylbis(benzimidazolium) diiodide (0.200 g, 0.366 mmol) [L] was prepared using the method reported by Bielawski et al. [23,26] and silver oxide (0.0850 g, 0.366 mmol) were added in THF (30 mL) under argon. The reaction flask was wrapped with an aluminum foil to avoid the light and heated at 70°C for 3 days. The reaction solution was then filtered from the residue and evaporated. The obtained solid was washed with water ($20\text{ mL} \times 2$) and pentane ($20\text{ mL} \times 2$) successively and dried in vacuo to give dark black solid (0.160 g, 57.5%). Alternatively, tetramethylbis(benzimidazolium) iodide [L] (0.500 g, 0.915 mmol) could be treated with sodium hydride (55 wt%, 0.080 g, 1.83 mmol) in toluene (30 mL) under the argon. After 3 h, stirring silver iodide (0.43 g, 1.83 mmol) was added to the reaction flask and the solution was heated at 70°C for 48 h under dark condition. The solution was finally filtered and evaporated. The obtained solid was washed with water ($20\text{ mL} \times 2$) and pentane ($20\text{ mL} \times 2$) successively and dried in vacuo to give dark black solid (0.403 g, 58.0%). ^1H NMR (400 MHz, DMSO-d_6): δ 7.47 (s, 2H), 7.41 (d, $J=3.9\text{ Hz}$, 2H), 7.21 (d, $J=4.0\text{ Hz}$, 2H), 3.40 (s, 6H), 3.25 (s, 6H). ^{13}C NMR (600 MHz, CDCl_3): δ 27.06 (2C), 54.49 (2C), 105.99 (2C), 107.81 (2C), 119.52(2C), 128.91 (2C), 130.37 (2C), 134.11 (2C), 154.10 (2C). IR (solid state,

cm^{-1}): 3416(m), 3057(m), 2918(m), 2850(m), 1665(w), 1569(s), 1491(s), 1443(s), 1384(s), 1264(m), 1155(w), 1093(w), 1031(w), 1009(w), 945(w), 843(m), 808(s), 792(s), 667(w), 594(w). Analysis calculated for $\text{C}_{18}\text{H}_{18}\text{N}_4\text{Ag}_2\text{I}_2$: C, 28.45%; H, 2.39%; N, 7.37%. Found: C, 28.37%; H, 2.65%; N, 7.35%. ICP (Ag): calculated: 28.39%. Found: 28.25%.

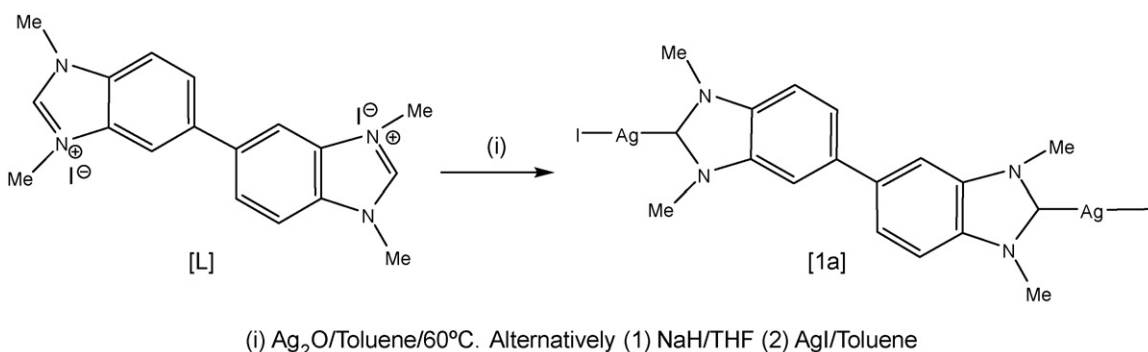
2.3. Electrochemical measurements

Ag complex dissolved in diethylamine was coated on Ag wire and a conventional three electrode systems were employed using the platinized Pt plate as counter and working electrodes to investigate its possible application as reference electrode. Cyclic voltammetry in acid (0.5 M H_2SO_4) and alkaline media (1.0 M NaOH) was performed using potentiostat/galvanostat (Autolab, PGSTAT1287N). To compare the potential shift of Ag/Ag complex reference electrode to that of the commercial standard reference electrodes, the experiments using Ag/AgCl/3 M KCl in acid and Hg/HgO in alkaline electrolyte were carried out. The Ag/Ag complex prepared as a reference electrode can be stored at room temperature with no further caution required.

3. Results and discussion

N-heterocyclic ligand [L] was first synthesized by cyclizing 3,3'-diaminobenzidine under formic acid to produce 3,3'-bibenzimidazole followed by the base treatment using 4 equiv. of MeI. Metallation was then accomplished by the addition of AgI under the base, NaH or alternatively by the reduction of Ag_2O by eliminating water with moderate yield. A simplified scheme showing the synthesis of silver (I) complex is depicted in Scheme 1. The complex [1a], despite of low solubility in organic solvent, was then characterized by ^1H NMR, ^{13}C NMR, UV/PL and elemental analysis. Successful synthesis of silver complex [1a] from the ligand [L] was demonstrated by the disappearance of distinctive hydrogen at the carbon of NHC ligand [L], which is shown at δ 9.72 in ^1H NMR. In addition, the ipso carbon of NHC ligand [L] at δ 144.77 in ^{13}C NMR was changed into δ 154.10. The electronic absorption spectra of ligand [L] and complex [1a] in DMSO has shown intensive absorption band at $\lambda_{\text{max}} = 296\text{ nm}$ ($\epsilon = 77,000\text{ M}^{-1}\text{ cm}^{-1}$) and $\lambda_{\text{max}} = 326\text{ nm}$ ($\epsilon = 21,000\text{ M}^{-1}\text{ cm}^{-1}$), respectively (Fig. 1(a)). The similar band shape and position of [L] and [1a] indicate that even the silver iodide substituted for the carbene hydrogen on NHC ligand [L], it barely changed the structure of complex. For the emission spectra, high-energy emission bands appear at $\lambda_{\text{max}} = 378\text{ nm}$ for the complex [1a] and at $\lambda_{\text{max}} = 348\text{ nm}$ for the ligand [L] with phenomenon of red shift (Fig. 1(b)).

Fig. 2(a) shows that SEM image of the prepared Ag complex [1a] represent well-dispersed small particle without agglomeration and formation of big lumps. Fig. 2(b) is powder XRD data of Ag



Scheme 1. Synthetic scheme for the silver (I) tetramethylbis(benzimidazolium) diiodide [1a] complex.

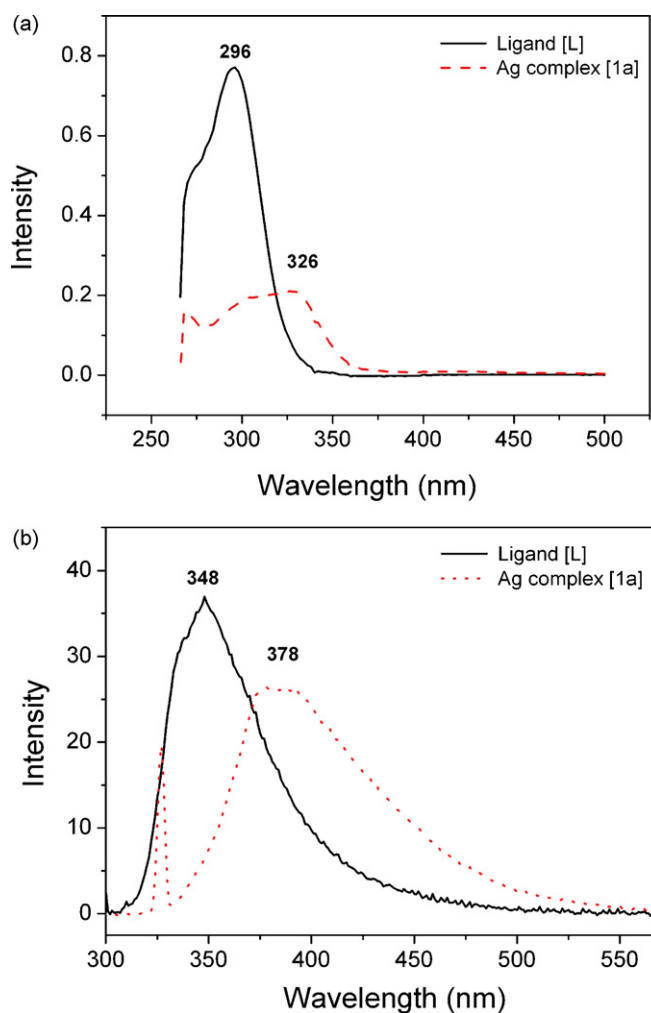


Fig. 1. UV (a) and emission (b) spectra of ligand [L] and silver (I) tetramethylbis(benzimidazolium) diiodide [1a].

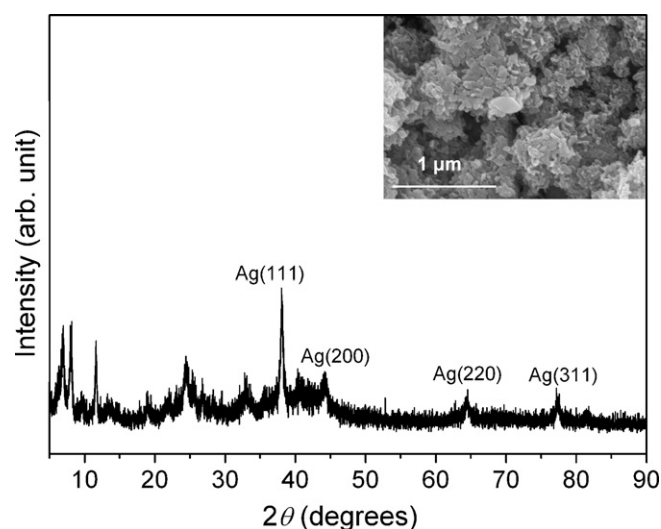


Fig. 2. XRD structure and inset figure of SEM image of the complex silver (I) tetramethylbis(benzimidazolium) diiodide [1a].

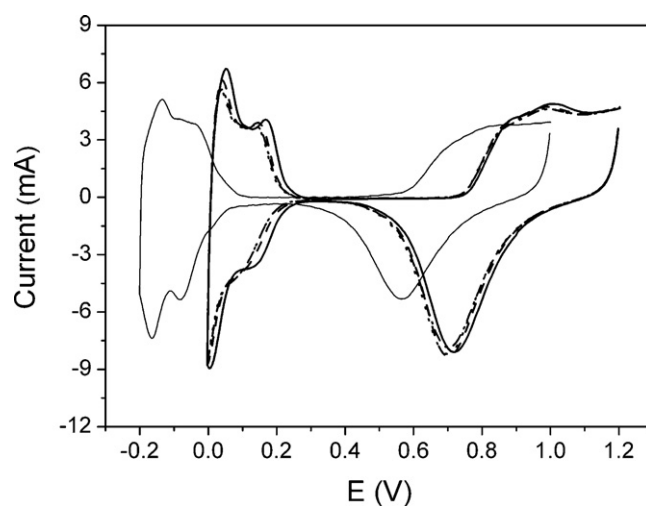


Fig. 3. Cyclic voltammograms of silver (I) tetramethylbis(benzimidazolium) diiodide [1a] used as a reference electrode in 0.5 M H_2SO_4 . Scan rate = 50 mV/s. Solid line: Ag/AgCl and bold line: 20 scans of Ag/Ag complex. Dotted lines: 30, 40 and 50 scans of Ag/Ag complex.

complex [1a] and its crystal structure shows dominant small angle peaks, which are comparable characteristic of N-alkylimidazole-silver complex [27]. Other relatively big angle peaks are assigned to (1 1 1), (2 0 0), (3 1 1) and (2 2 0) reflections.

The well-characterized Ag complex was finally tested as a reference electrode in both acid and alkaline electrolysis using cyclic voltammetry. Fig. 3 presents cyclic voltammograms of Pt with a reference electrode of the silver complex in 0.5 M H_2SO_4 solution. In order to verify the stability and reproducibility of the Ag complex as a reference electrode compared commercial Ag/AgCl electrode, over 50 cycles of cyclic voltammograms (CVs) of Pt were obtained using Ag/Ag complex RE. The voltammogram results show good reproducibility on achieving a higher oxygen adsorption/desorption charge on Pt surface sites compared to that of commercial Ag/AgCl RE after compensation of the oxygen onset potential shift. The difference between Ag/AgCl (3 M KCl) and standard hydrogen electrode (SHE) reference electrodes is about 0.197 V and thus we generally measured the hydrogen under potential deposition/oxidation and (hydro)oxide formation and

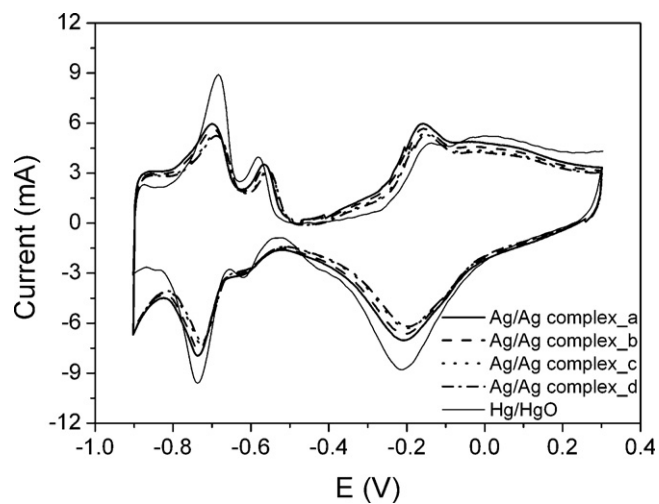


Fig. 4. Cyclic voltammograms of silver (I) tetramethylbis(benzimidazolium) diiodide [1a] used as a reference electrode in 1.0 M NaOH. Scan rate = 50 mV/s. The cycle was repeated up to 800 times for a week. Solid line: Hg/HgO. Ag/Ag complex_a, b, c and d are 500, 600, 700 and 800 scans of Ag/Ag complex, respectively.

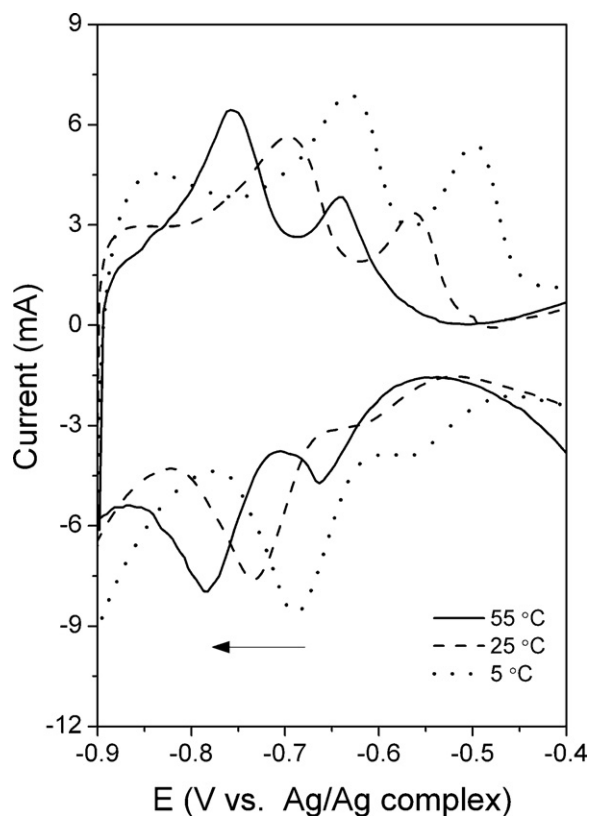


Fig. 5. Cyclic voltammograms of silver (I) tetramethylbis(benzimidazolium) diiodide [1a] used as a reference electrode in 1.0M NaOH at different temperatures of the solution ranging from 5 °C to 55 °C. Scan rate = 50 mV/s. Solid line: 55 °C, dashed line: 25 °C and dotted line: 5 °C.

desorption between -0.2 V and 1.0 V. However, potential window corresponding hydrogen and oxidation behaviors on Pt with Ag/Ag complex reference is between almost 0 V and 1.2 V, which is found to be very similar to CVs obtained with the standard hydrogen reference electrode (SHE). The Ag/Ag complex as a metal reference electrode was further tested in acidic media ranging from pH 0 to 4 and showed little changes in the potential of hydrogen adsorption/desorption. In addition, the Ag/Ag complex RE showed still excellent stability to continue to measure CVs of Pt in acidic media over 100 cycles.

In order to evaluate Ag/Ag complex that can be used as reference electrode in an alkaline media, the cyclic voltammetry of Pt electrode was performed in 1.0M NaOH solution as shown in Fig. 4. The potential differences between Ag/Ag complex and SHE in acidic media and in alkaline media are 0.05 V and 0.027 V, respectively. The initial voltammogram of Pt shows unstable curve due to the change of Ag complex into Ag oxide. After 10 cycles of CV, a stable current–potential profile was achieved and this cycle was repeated up to 800 times for 2 days without any significant changes in the profile. Excellent reproducibility of hydrogen adsorption/desorption on the Pt working electrode with respect to the silver/silver complex electrode was observed and the adsorp-

tion/desorption behavior was similar to that obtained using the conventional Hg/HgO reference electrode. The pH changes in alkaline media from 10 to 14 were also found to have little effect on the potential value of hydrogen adsorption/desorption (data not shown). Moreover, we investigated the effect of solution temperature on the reference electrode performance. As can be seen in Fig. 5, the adsorption peak on the cathodic scan shifted linearly toward more negative potential as the temperature increased [1–3]. This indicates that the Ag/Ag complex electrode could be used as a reference electrode in alkaline media at a temperature range from 5 °C to 55 °C.

4. Conclusions

The organic–inorganic hybrid silver complex, namely, silver (I) tetramethylbis(benzimidazolium) diiodide were successfully synthesized and well-characterized. This complex exhibits excellent electrochemical characteristics as a reference electrode in both acid and alkaline solution with superb stability and reproducibility. We envision that the Ag complex (I) could potentially replace the conventional Ag/AgCl electrode systems in acidic media and Hg/HgO electrode systems in alkaline media electrolysis.

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