ORGANOMETALLICS

Decamethylferrocene Redox Chemistry and Gold Nanowire Electrodeposition at Salt CrystallElectrodelNonpolar Organic Solvent Contacts

John D. Watkins, Christopher E. Hotchen, John M. Mitchels, and Frank Marken*

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

ABSTRACT: This report describes exploratory experimental findings for electrochemical processes in nonpolar solvents (hexane, toluene, and dichloroethane). Conventional 3 mm diameter glassy-carbon-disk electrodes are used in contact with a crystalline salt electrolyte (ammonium nitrate) immersed in nonpolar solvents. The insoluble salt is employed as a "surface thin film electrolyte", with humidity causing electrical connection from the working electrode to the SCE counterreference electrode. The organic solvents are employed without intentionally added electrolyte. Humidity in the nonpolar solvents is shown to be essential for the processes to work. The oxidation of decamethylferrocene is demonstrated as a test organometallic redox system. The electro-



chemical reduction of Au(III) in toluene (solubilized with tetraoctylammonium bromide, TOABr) is employed to demonstrate and visualize the reaction zone around salt crystallworking electrode contact points. Gold nanowire bundle formation is observed, presumably due to an ordered interfacial surfactant microphase at saltlelectrode contact points. The triple phase boundary nature of these processes is discussed, and future applications are suggested.

■ INTRODUCTION

Electrochemical processes for the conversion of organic or organometallic redox systems in nonpolar solvents are important and desirable even in highly nonpolar media such as fluorohydrocarbons,¹ toluene,² oils,³ and heptane.⁴ New methods have been developed, for example, on the basis of novel nonpolar solvent soluble and sufficiently dissociated electrolyte salts or ionic liquids,^{5,6} on the basis of liquid–liquid triple phase boundary reactor systems⁷ where electrolytic conduction is required only in the polar phase,^{8,9} and on the basis of particle supported (heterogeneous) electrolyte systems such as pyridinium-substituted polymer beads.^{10,11} The last technology allowed substantial currents to be passed and bulk product to be generated with a heterogeneous supporting electrolyte system that is readily recovered by filtration and reused. In the work presented here, a heterogeneous supporting electrolyte system is proposed on the basis of insoluble salt (ammonium nitrate) crystals in contact with the working electrode surface and surrounded by the nonpolar reagent media.

Figure 1A shows a schematic drawing with a salt crystal in contact with a glassy-carbon-electrode surface. In a dry nonpolar solvent environment there would be no significant ionic conductivity and therefore electrochemical processes are difficult to observe. However, when the solvent is saturated with water before use (mutual solubilities at 298 K are $x_2 = 6 \times 10^{-4}$ or 4.6 mM for water in hexane,¹² 3×10^{-3} or 28 mM for water in toluene,¹³ and 10×10^{-3} or 130 mM for water in



Figure 1. Schematic representation of (A) a salthonpolar solventl electrode contact and (B) the electrochemical cell with humidified nonpolar solvent flowing through the salt.

dichloroethane¹⁴), the surface of the salt crystals (here ammonium nitrate) will be equilibrated and coated with a thin water layer sufficient for ion conductivity to be achieved. The cation C^+ , the anion A^- , or additional ions such as protons H^+ are likely to contribute to the charge transport (see Figure 1A) and the overall process. In the vicinity of the contact point of the salt with the electrode surface various types of redox processes become possible, including processes involving redox-active reagents dissolved in the nonpolar solvent.

Special Issue: F. Gordon A. Stone Commemorative Issue

Received: July 9, 2011 Published: January 10, 2012

Organometallics

In recent reports the use of saltlelectrode contact processes has been demonstrated for the case of salt surface immobilized redox systems,¹⁵ for palladium catalyst coated electrodes,¹⁶ and for textile-coated electrodes.¹⁷ In this study it is demonstrated that ammonium nitrate salt crystals can be used as a "thin film electrolyte phase" also in a nonpolar solvent such as hexane to electrically connect the working electrode and a counterreference electrode (see Figure 1B). The resulting saltlelectrode contact points allow solvent flow experiments and provide unique reaction environments for redox processes, involving for example decamethylferrocene metal complexes, as well as for bulk metal deposition from a Au(III) precursor solution in toluene. The key aims of this study are (i) to demonstrate redox processes in nonpolar solvents such as hexane and toluene, (ii) to introduce saltlnonpolar solventlelectrode contacts for electrochemical processes, and (iii) to employ gold electrodeposition in order to visualize localized activity and nanoscale pattern formation on electrode surfaces.

RESULTS AND DISCUSSION

Oxidation of Decamethylferrocene at Salt | Electrode Contacts. *I. Processes in Hexane.* Decamethylferrocene is a well-known one-electron-redox system with good solubility in nonpolar media such as hexane.¹⁸ The redox chemistry of decamethylferrocene has been studied in the past in solution,¹⁹ as a solid immersed in aqueous media,²⁰ and in liquidlliquid environments.^{21,22} Here decamethylferrocene is dissolved into hexane (humidified but without any added electrolyte) and investigated at saltlglassy-carbon working electrode contacts. Figure 2A shows a typical set of cyclic voltammograms obtained



Figure 2. Cyclic voltammograms (scan rate (i) 10, (ii) 20, (iii) 50, and (iv) 100 mV s⁻¹) for (A) the oxidation and back-reduction of 2 mM decamethylferrocene in humidified hexane in contact with NH_4NO_3I glassy carbon, (B) as for (A) but in toluene, (C) as for (A) but in dichloroethane.

for 2 mM decamethylferrocene in hexane (humidified) under no-flow conditions. A clear oxidation and back-reduction redox cycle is observed centered at $E_{\rm mid} = 1/2(E_{\rm p}^{\rm ox} + E_{\rm p}^{\rm red}) = 0.16 \text{ V}$ vs SCE, with a clear separation between the oxidation and the reduction peaks. The oxidation product, decamethylferrocenium cations, is insoluble in hexane and assumed to precipitate here in the form of a nitrate salt (see eq 1).

$$FeCp*_{2}(hexane) + NO_{3}^{-}(salt)$$

$$\approx FeCp*_{2}^{+}NO_{3}^{-}(solid) + e^{-}(electrode)$$
(1)

The shape of the voltammetric peak responses is symmetric at lower scan rates (10 mV s⁻¹ and less), and the absence of a "diffusional tail" is observed for both the oxidation and the back-reduction. For the oxidation the formation of the product $FeCp_2^{*+}NO_3^{-}$ (solid) as a precipitate in the electrochemically active region of the electrode is likely to lead to electrode blocking and thin film behavior (vide infra). During the back-reduction the solid precipitate redissolves. The separation of the oxidation and back-reduction peaks (hysteresis) is due here to the formation of the new solid phase.

When the scan rate is increased, the peak currents for both oxidation and back-reduction increase while the charge under the voltammetric response decreases with higher scan rate. The shape of these voltammetric responses can be seen to be affected by uncompensated iR-drop phenomena with an estimated resistivity of 70 k Ω (see Figure 2A inset). This resistivity is likely to be localized predominantly in the salt electrolyte connecting the working and the counter-reference electrode. However, contributions from the hexanelsaltl electrode triple phase boundary are also possible (vide infra). An important parameter in this experiment is the humidity level in the organic solvent. When the experiment is conducted with dry hexane, there are no significant currents observed. Also, when the experiment is conducted in wet solvent without salt, no significant currents are observed. In contrast, watersaturated hexane (containing ca. 4.6 mM water¹²) allows sufficient ion conduction at the saltlorganic solvent interface to occur.

II. Comparison of Hexane, Toluene, and Dichloroethane. In order to explore the reactivity of decamethylferrocene in other nonpolar solvent media under the same saltlelectrode contact conditions, experiments were performed with toluene and with dichloroethane. Figure 2B shows typical voltammetric responses for the oxidation of 2 mM decamethylferrocene in toluene as a function of scan rate. At lower scan rates peak-shaped responses are observed with a midpoint potential of ca. $E_{\rm mid} = 0.17$ V vs SCE. The process is very similar to that observed in hexane, and therefore a similar mechanism is suggested (eq 2).

$$FeCp*_{2}(toluene) + NO_{3}^{-}(salt)$$

$$\approx FeCp*_{2}^{+}NO_{3}^{-}(solid) + e^{-}(electrode)$$
(2)

The charge under the voltammetric peaks in toluene (humidified) is similar to that for the hexane process, and the effect of resistivity appears similar. In contrast, when the process is investigated in dichloroethane (humidified), a more reversible voltammetric response is observed (see Figure 2C). Oxidation and back-reduction peaks are less separated and the midpoint potential is ca. $E_{\text{mid}} = -0.02$ V vs SCE. The negative shift in the midpoint potential is likely to be caused by the higher solubility of the product FeCp*₂⁺ in dichloroethane (DCE), and a modified mechanism is proposed (eq 3).

$$FeCp*_{2}(DCE) + NO_{3}^{-}(salt)$$

$$\approx FeCp*_{2}^{+}(DCE) + NO_{3}^{-}(DCE)$$

$$+ e^{-}(electrode)$$
(3)

Voltammetric responses in dichloroethane do exhibit a typical "diffusional tail" in the current, and an analysis of the charge under the peaks suggests planar diffusion of product away from the reaction zone (no formation of precipitate; vide infra). Therefore, in this case a comparison of the experimental peak current with the theoretically expected peak current is possible. The theoretical peak current (for planar diffusion to a flat electrode) as a function of scan rate is given by the Randles-Sevcik expression²³ (see eq 4), where the peak current $I_{\rm p}$ is related to the number of transferred electrons per molecule diffusing to the electrode surface, n, the Faraday constant, F, the gas constant, R, the absolute temperature, T, the scan rate, v, the electrode area, A (without taking into account partial blocking of the electrode by salt crystals; vide infra), the diffusion coefficient, D, and the concentration of redox-active material, c.

$$I_{\rm p} = 0.446 n FAc \sqrt{\frac{n F \nu D}{RT}}$$
(4)

For decamethylferrocene in dichloroethane the diffusion coefficient estimated with the Wilke–Chang expression²⁴ is 0.7 $\times 10^{-9}$ m² s⁻¹ (at 293 K) and therefore the expected peak current at 10 mV s⁻¹ scan rate is $I_p = 10 \ \mu$ A. The measured peak current is only 2 μ A, suggesting that only approximately 20% of the area of the glassy-carbon electrode surface is active. The remaining 80% of the electrode area is either blocked by salt crystals or is too far from the salt contacts and remains inactive. The extent of the "active zone" in this experiment is dependent on the salt crystal size and shape or coverage at the electrode surface. A summary of the effect of the solvent on the voltammetric response is shown in Figure 3A. Both the peak-topeak separation and the resistivity effect are changed on going from highly nonpolar (hexane, toluene) to modestly nonpolar (dichloroethane) solvent systems.

The effect of the decamethylferrocene concentration on the voltammetric response is shown in Figure 3B for the case of hexane solutions. The precipitation mechanism is responsible for a nonlinear correlation, with higher concentrations causing slightly sharper peaks without an increase in area under the peak. The shape of the peaks also suggests a decrease in resistivity upon increasing the decamethylferrocene concentration. This as well as the considerable overpotential for oxidation at lower concentrations is associated with the precipitation mechanism, where a higher concentration (or more correctly a higher activity) may allow a more rapid precipitation closer to the saltlelectrode contact region. Nonpolar solvent contributions to the resistivity in the triple phase boundary region seem possible under these conditions.

Next, the effect of solvent flow on the voltammetric responses is investigated. A syringe pump was employed for a flow of 400 μ L min⁻¹ of solvent through the salt layer (see Figure 1B). Perhaps surprisingly, the flow did not affect the voltammetric responses for hexane and toluene (not shown). Peak-shaped oxidation and back-reduction responses were observed in both cases. Therefore, the flow-induced diffusion layer thickness change was ineffective in preventing the precipitation process. However, for the dichloroethane system



Figure 3. (A) Cyclic voltammograms (scan rate 10 mV s⁻¹) for the oxidation of 2 mM decamethylferrocene in humidified (i) hexane, (ii) toluene, and (iii) dichloroethane obtained at a NH₄NO₃ saltlglassy-carbon electrode contact. (B) Cyclic voltammograms (scan rate 10 mV s⁻¹) for the oxidation of (i) 1 mM, (ii) 2 mM, and (iii) 5 mM decamethylferrocene in hexane. (C) Cyclic voltammograms (scan rate 10 mV s⁻¹) for the oxidation of 2 mM decamethylferrocene in dichloroethane in (i) static and (ii) flowing solution at 400 μ L min⁻¹.

an increase in current and a change from peak-shaped to sigmoidally shaped current response is seen (Figure 3C). Liquid flowing out from the cell exhibits a green color, as expected for the oxidized decamethylferrocenium. These observations confirm the proposed mechanism in eq 3.

Reduction of Au(III) to Gold Nanowires at Saltl Electrode Contacts. In order to investigate the reaction zone formed when NH₄NO₃ salt crystals are in contact with the glassy-carbon electrode surface, additional experiments were conducted employing a gold electrodeposition approach. In order to visualize the electrochemically active zone for saltl electrode contact points, a deposition from a toluene solution of Au^{III}Cl₄⁻ was chosen. Tetraoctylammonium bromide as a phase transfer reagent was employed to transfer tetrachloroaurate with a final concentration of 1 mM AuCl₄⁻ and 5 mM tetraoctylammonium bromide in toluene. Voltammetric responses (not shown) suggest highly resistive conditions. In order to achieve a gold deposition current of ca. 10 μ A, a potential of -3 V vs SCE was applied and the deposition continued for 30 min.

SEM imaging of the resulting electrode surface after rinsing (with acetone and water) and drying shows a characteristic pattern with the outline of salt crystals (ca. $10-100 \ \mu m$ in size) clearly visible (see Figure 4B). Energy-dispersive X-ray analysis confirmed the presence of a gold deposit (not shown). Perhaps surprisingly, the gold deposits exhibit a fine structure. Closer inspection (see Figure 4D) shows bundles of nanowires with individual filaments of less than 10 nm diameter. The mechanism is similar to that for the recently discovered surfactant template induced gold nanowire formation²⁵ and related to the nanostructure electrodeposition in lyotropic media pioneered by Attard et al.²⁶ The process can be explained on the basis of a liquid crystal phase domain formed in the vicinity of the salt crystals in the presence of humidity



Figure 4. SEM images for gold deposits formed at -3 V vs SCE at NH₄NO₃lelectrode contact points with ca. 10 μ A deposition current and 30 min deposition time in 1 mM AuCl₄⁻ and 5 mM tetraoctylammonium bromide in toluene (see the Experimental Section).

and tetraoctylammonium bromide (eq 5).

AuCl₄ (toluene) + 3e (electrode)

$$\Rightarrow$$
 Au(nanowire) + 4Cl⁻(toluene) (5)

The reaction zone is predominantly localized around regions where salt crystals contacted the electrode surface. Lines of good contact can be observed, and these indicate where the ammonium nitrate crystals interacted with the glassy carbon. The estimate of ca. 20% active electrode area (from voltammetry data; vide supra) can now be rationalized with this image (Figure 4B). Active electrode zone information from the gold deposit in conjunction with an assumed average diffusion path of ca. $\delta = (DRT/vF)^{1/2} = 42 \ \mu m$ (see parameters in eq 4) suggests that a substantial part (more than 20%) of the solution phase close to the electrode surface can be accessed. Electrode blocking due to salt crystals appears therefore likely to be the main reason for suppressed currents in data presented in Figure 2C.

Potential applications of the localized or patterned electrodeposition of gold nanowires could be in sensor and electronic component fabrication. The ammonium nitrate salt crystals could be replaced by other surface ion conductor materials to allow more precise control of the patterning process and of the conditions at the contact point. Gold could be replaced by other types of metal or nonmetal precursors. Potential future applications of the nonpolar solventlsaltlelectrode interface could also be in flow sensing (e.g., in oils, nonpolar media, supercritical or gas media).

CONCLUSIONS

It has been shown that electrochemistry in highly nonpolar solvent media such as hexane is possible at salt/solvent/electrode triple phase boundary contact points in the presence of sufficient levels of humidity. The oxidation of decamethylferrocene has been demonstrated and investigated as a mechanism involving precipitation in highly nonpolar media. The shape of voltammetric responses (static and with solvent flow) changes considerably when precipitation is avoided in dichloroethane solvent. The visualization of the triple phase boundary reaction zone was possible with a gold electrodeposition from toluene solution. Gold nanowire formation was observed in the presence of a surfactant template based on tetraoctylammonium bromide and humidity at the saltlelectrode contact.

In the future, the effects of the salt crystal grain size, singlecrystal salt contacts with electrodes, and the nature of the salt on the electrochemical process (e.g., localized pH control or direct supply of reagents) need to be studied in more detail. New types of electrochemical processes will be possible in media such as nonpolar oils, with a considerable range of applications.

EXPERIMENTAL SECTION

Chemical Reagents. Ammonium nitrate (\geq 99%, Sigma Aldrich), gold(III) trichloride (99.999%, Aldrich), hydrochloric acid (reagent grade, Fisher Scientific), tetraoctylammonium bromide (Aldrich, 98%), decamethylferrocene (Aldrich, 97%), 1,2-dichloroethane (Aldrich, GC grade, 99%), toluene (Sigma Aldrich, HPLC grade), and hexane (Fisher, HPLC grade) were obtained and used without further purification. Filtered and demineralized water was taken from a Millipore water purification system with not less than 18 M Ω cm resistivity.

Instrumentation. For voltammetric studies a microAutolab III potentiostat system (EcoChemie, Utrecht, The Netherlands) was employed with a KCl-saturated calomel (SCE) counter/reference electrode (Radiometer, Copenhagen, Denmark). The working electrode was a 3 mm diameter glassy-carbon disk (BAS). The surface morphology and topology of the films were observed using a JEOL JSM6480LV scanning electron microscope and a JEOL JSM6301F field emission scanning electron microscope. All experiments were conducted at 22 ± 2 °C.

Procedure I: Salt Cell Experiments. To prepare the electrochemical cell, ca. 1 g of ammonium nitrate was ground using a pestle and mortar into a finely divided powder (10–100 μ m particles). This powder was then loaded into the cell onto the counter-reference (see Figure 1B) from the working electrode side. The working electrode was then gently screwed down to compact the powder into a solid cake with a good electrical contact between the powder and both the working and counter/reference electrode. The organic solvent (hexane, toluene, or dichloromethane, pre-equilibrated with water) containing a redox probe was then flowed through the cell from the side with a syringe pump. Experiments were conducted without flow or with typically 400 μ L min⁻¹ solution flow rate.

Procedure II: Salt Cell Gold Electrodeposition Experiments. Gold deposition experiments were carried out using a 1 mM solution of tetrachloroaurate/5 mM tetraoctylammonium bromide in toluene under static conditions. The solution was prepared following a recipe by Brust et al.²⁷ A 3 mL volume of a solution of 30 mM of hydrogen chloride and 30 mM gold(III) trichloride was added to 8 mL of a solution of 50 mM tetraoctylammonium bromide in toluene. The mixture was shaken and left to equilibrate for several minutes until the aqueous layer (bottom) became decolorized and the toluene layer (upper) became bright red. The toluene layer was recovered by syringe and diluted with 80 mL of toluene to give a solution with ca. 1 mM Au(III) and ca. 5 mM tetraoctylammonium bromide. The deposition potential in the salt cell was chosen to provide roughly 10 μ A of current (ca. -3 V vs SCE). The electrodeposition of gold was carried out for 30 min (under no-flow stationary conditions), after which the electrode was removed, thoroughly rinsed with acetone and distilled water, and dried. Gold deposits were seen by optical microscopy and further confirmed by EDS and SEM imaging methods.

AUTHOR INFORMATION

Corresponding Author

*E-mail: F.Marken@bath.ac.uk.

ACKNOWLEDGMENTS

Charles Y. Cummings is gratefully acknowledged for help with SEM imaging. J.D.W. thanks the EPSRC for support through a DTA studentship.

DEDICATION

Dedicated to the memory of Gordon Stone, an inspiring chemist, leader, and pioneer.

REFERENCES

(1) LeSuer, R. J.; Geiger, W. E. J. Electroanal. Chem. 2006, 594, 20-26.

(2) Oldham, K. B.; Cardwell, T. J.; Santos, J. H.; Bond, A. M. J. Electroanal. Chem. 1997, 430, 39-46.

(3) Oliveri, P.; Baldo, M. A.; Daniele, S.; Forina, M. Anal. Bioanal. Chem. 2009, 395, 1135–1143.

(4) Bond, A. M. Analyst 1994, 119, R1-R21.

(5) Cardwell, T. J.; Santos, J. H.; Bond, A. M. Anal. Chim. Acta 1997, 340, 169–174.

(6) Duffy, N. W.; Bond, A. M. Electrochem. Commun. 2006, 8, 892–898.

(7) MacDonald, S. M.; Watkins, J. D.; Bull, S. D.; Davies, I. R.; Gu,

Y.; Yunus, K.; Fisher, A. C.; Page, P. C. B.; Chan, Y.; Elliott, C.; Marken, F. J. Phys. Org. Chem. **2009**, 22, 52–58.

(8) Banks, C. E.; Davies, T. J.; Evans, R. G.; Hignett, G.; Wain, A. J.; Lawrence, N. S.; Wadhawan, J. D.; Marken, F.; Compton, R. G. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4053–4069.

(9) Marken, F.; Watkins, J. D.; Collins, A. M. Phys. Chem. Chem. Phys. 2011, 13, 10036–10047.

(10) Tajima, T.; Fuchigami, T. J. Am. Chem. Soc. 2005, 127, 2848–2849.

- (11) Kurihara, H.; Fuchigami, T.; Tajima, T. J. Org. Chem. 2008, 73, 6888–6890.
- (12) Maczynski, A.; Shaw, D. G.; Goral, M.; Wisniewska-Goclowska, B.; Skrzecz, A.; Owczarek, I.; Blazej, K.; Haulait-Pirson, M. C.; Hefter, G. T.; Kapuku, F.; Maczynska, Z.; Young, C. L. J. Phys. Chem. Ref. Data **2005**, 34, 709–754.
- (13) Neely, B. J.; Wagner, J.; Robinson, R. L.; Gasem, K. A. M. J. Chem. Eng. Data 2008, 53, 165-174.
- (14) Horvath, A. L.; Getzen, F. W.; Maczynska, Z. J. Phys. Chem. Ref. Data 1999, 28, 395-627.
- (15) Dale, S. E. C.; Cummings, C. Y.; Marken, F. Electrochem. Commun. 2011, 13, 154–157.
- (16) Xia, F.; Dale, S. E. C.; Webster, R. A.; Pan, M.; Mu, S. C.; Tsang,
- S. C.; Mitchels, J. M.; Marken, F. New J. Chem. 2011, 35, 1855–1860.
 (17) Shariki, S.; Dale, S. E. C.; Marken, F. Electroanalysis 2011, 23, 2149–2155.
- (18) Saczek-Maj, M.; Opallo, M. Electroanalysis 2002, 14, 1060-1066.
- (19) Wang, H.; Zhao, C.; Bhatt, A. I.; MacFarlane, D. R.; Lu, J. X.; Bond, A. M. ChemPhysChem **2009**, *10*, 455–461.
- (20) Bond, A. M.; Marken, F. J. Electroanal. Chem. 1994, 372, 125–135.
- (21) Bak, E.; Donten, M.; Stojek, Z. J. Electroanal. Chem. 2007, 600, 45-53.
- (22) Mirceski, V.; Quentel, F.; L'Her, M.; Scholz, F. J. Electroanal. Chem. 2006, 586, 86–97.

(23) Scholz, F. Electroanalytical Methods; Springer: Berlin, 2002; p 64.
(24) Wilke, C. R.; Chang, P. AIChE J. 1955, 1, 264–270.

(25) Azulai, D.; Belenkova, T.; Gilon, H.; Barkay, Z.; Markovich, G. Nano Lett. 2009, 9, 4246-4249.

- (26) Attard, G. S.; Bartlett, P. N.; Coleman, N. R. B.; Elliott, J. M.; Owen, J. R.; Wang, J. H. Science **1997**, 278, 838-840.
- (27) Brust, M.; Walker, M.; Schiffrin, D. J.; Whyman, R. J. Chem. Soc., Chem. Commun. **1994**, 801–802.