Preliminary Investigations for the Application of Composite Electrodes in Organic Electrosynthesis

Dezso Szikra, Timea Varadi and Istvan P. Nagy

Department of Physical Chemistry, University of Debrecen, P.O.Box 7, H-4010 Debrecen, Hungary

Received: April 07, 2008, Accepted: July 06, 2008

Abstract: Electrodes made of conductive composites of acrylamide and triethylene glycol dimethacrylate with various graphite content have been tested as electrodes in organic electroreduction. Electrochemical properties of the composite electrodes can be varied and controlled by changing their composition. Several parameters, such as conversion, current efficiency, and chemoselectivity of the electroreduction have been found to be affected by the graphite content.

Keywords: frontal polymerization, composite electrode, acetophenone, electroreduction

1. INTRODUCTION

On the basis of former results of our laboratory [1], we focus on the development of new electrode materials for electrochemical syntheses. We use frontal polymerization for preparation of the composites. This is a special mode of polymerization in which a localized zone of reaction propagates in an unstirred medium driven by the heat evolution of the reaction [2]. Frontal polymerization has several potential advantages over homogeneous phase methods. High temperature (over 200 °C) accelerates the reaction, and enables the synthesis of products that would phase-separate and sediment if the reaction time was longer. Fast and cheap polymer preparation facilitates the optimization of copolymer composition.

The monomers used in our work are typically acrylic acid derivatives, mainly acrylamide (AA) and triethylene glycol dimethacrylate (TGDMA). The polymers obtained are highly crosslinked and withstand numerous solvents for weeks.

Several additives may be incorporated into the polymer matrix in order to obtain product with desired features. For example graphite powder converts the composite into an electrically conductive material [1], which might be of great practical importance. The electrical resistivity of 10-40 w% graphite containing composites varies from 9.3·10^7 to 4.8·10^5 Ohm·mm²/m. Such a resistivity makes it possible to use these composites in organic electrosynthesis. We prepared electrodes out of these composites and studied their behaviour in electrosynthesis.

The electroreduction of acetophenone was chosen as a test reaction. The two main products obtained by one- and two-electron reduction are 2,3-diphenyl-2,3-butanediol and 1-phenylethanol, respectively. Several factors have influence on product composition: cathode potential, protic or aprotic conditions, pH, conducting salt, material and morphology of the electrode.

Different values of DL/meso-pinacol ratio in acid or alkaline solutions indicate different dimerization mechanisms in the two media [3]. At low pH, dimerization proceeds by the combination of two neutral radicals because the same diastereoselectivity was found in the photopinacolization of acetophenone [4].

In alkaline solution most of the radicals formed as anions and react with the neutral radicals present in small amount. Hydrogen bonds are stronger between the negatively charged oxygen of the anion and the hydroxyl group of the neutral radical, resulting in preference of DL pinacol formation. Because of repulsive forces between anions their coupling is slower [3].

Elving and Leone assume an alternative path of radical generation, in which the reduction of acetophenone is preceded by protonation or hydrogen bond formation [5].

Tilborg and Smit examined the role of adsorption of acetophenone and quaternary ammonium salts in the mechanism of electroreduction in aqueous [6] and aprotic media [7]. They concluded on the basis of their results that in aqueous media acetophenone is reduced on top of an adsorbate layer of tetraalkylammonium ions. Under strictly anhydrous conditions acetophenone can be reduced only if tetraalkylammonium ions are...
present. Their catalytic effect is ascribed to the increased polarization of the carbonyl bond, induced by coordination of the ammonium ions.

In dry aprotic solvents the radical anions form ion pairs with the cations being present. If the cation interacts with two radicals simultaneously, the stabilization effect is the same as that of hydrogen bonding in the transition state in this case the DL-pinacol appears to be the main product. Tetraethylammonium bromide as conducting salt in acetonitrile [8] or magnesium ions formed in the dissolution of sacrificial magnesium anode [9] are capable of enhancing diastereoselectivity toward the DL-pinacol.

Ion pair formation can be responsible for the asymmetric induction found in the presence of optically active conducting salts [10].

In neutral or weakly alkaline aqueous media acetophenone is reduced to alcohol in a single 2-electron wave. With increasing acetophenone concentration dimerization of the neutral or anionic radicals becomes predominant [11]. Stirring plays an important role in determining the chemoselectivity of the reaction. Efficient stirring enhances the transfer of the electrogenerated radicals to the bulk of the solution preventing their further reduction and enhancing pinacolization. Accomplishment of stirring by the aid of ultrasound besides mixing helps to keep the electrode surface clean which suppresses changes in electrode potential during electrolysis [12][13].

Effect of acetophenone concentration on chemoselectivity can be used to increase the product ratio of phenylethanol by performing the electroreduction in the ternary system of water/toluene/acetophenone emulsified by sonication. The low concentration of acetophenone in the aqueous phase plays down the pinacolization [14].

Electrode surface and its modification plays an important role in changing the selectivity of the reduction. An interesting observation is that chemoselectivity and diastereoselectivity are influenced by surface modification of the electrode. Ishifune et al [15][16] has anodically oxidized carbon fibre and introduced β-cyclodextrin onto the surface. Both modified electrode enhanced the formation of the DL-pinacols which can be explained by interactions of the surface hydroxyl groups with the intermediate radicals.

On graphite and mercury electrodes the pinacol is obtained as the main product, while in the case of nickel in protic media the selectivity is inverted [17]. Using platinised platinum electrodes, etilbenzene is found to be the main product [18]. Numerous authors examined the electroreduction of acetophenone. For example, Swann [19], Elving and Leone [5], and Horner et al. [20]. In their work product analysis has been carried out after various procedures consisting of distillation, extraction or crystallization thus the results are not comparable to each other. Janssen [21] examined the reduction products directly by HPLC. He has studied the effects of several parameters, using graphite cathode. In water-ethanol mixtures containing 0.2 M H₂SO₄ he has not found any effect of cathode potential, or water content (between 5 and 40%) on diastereoselectivity. The nature of the examined supporting electrolytes has not altered the DL/meso ratio, but changing the alcohol from methanol to isopropanol increased it from 1.02 to 1.24. The pH of the electrolyte had the greatest effect on diastereoselectivity. The DL/meso ratio increased form 1.1 to 3.3 for a pH increase from 1 to 14. In alkaline solutions practically no phenylethanol was formed.
2. EXPERIMENTAL

2.1. Chemicals used for composite preparation

Acrylamide (purum), from Sigma-Aldrich was ground in a ball-mill for 12 hours. Graphite (Merck, >95%) 50 µm powder, triethylene glycol dimethacrylate (>95%) and α,α′-azoisobutyronitrile (>98%) from Fluka were used as received. Acetophenone and dimethylformamide were distilled prior to use. Lithium bromide was dried at 110 °C.

2.2. Preparation of composites

The monomers, additives, and initiator are homogenized in a mortar and filled into a test tube (9 mm diam., 100 mm length). The polymerization started on the top of the mixture with thermal initiation by means of a soldering iron. The polymerization front travels through the monomer mixture and leaves the product behind. The solidifying material slightly expands and the reaction takes place under overpressure suppressing bubble formation. This way the product has better structural and mechanical properties than bulk polymerized composites.

The composite rods are removed from the test tube and cut to 5 mm thick slices by a diamond cutting wheel. Copper wire is curled round the composite disk and isolated with thermoplastic polymer from a glue gun.

2.3. Resistance measurement

The resistance of a composite sample is measured by an ohmmeter connected to two polished copper disks between which the sample is squeezed. Compression force is increased until constant reading of resistance is reached.

2.4. Electrosynthesis

Electrochemical experiments were performed using a home-built potentiostat connected to a Cole-Parmer 18200-10 data acquisition module. The performance of the potentiostat was tested using ferrocene as redox probe. Preparative electrolysis were carried out potentiostatically in a two compartment U-cell divided by a glass frit with working volume of 2 ml for the catholyte. Composite working electrodes had a geometrical surface area of 0.64 cm². The cell was filled with 0.3 M LiBr solution in water – DMF 1:1, and 5 µl acetophenone was added to the catholyte. Saturated calomel electrode was used as reference in a Luggin-capillary and platinum as auxiliary electrode. Catholyte was stirred by means of a small magnetic stirring bar.

Product analysis was performed by HPLC. Waters Xterra RP18 5 µm, 4.6x150 mm column, eluent: acetonitrile/water 35/65, flow: 1 ml/min. Detection: 220 nm. 10 µl catholyte was injected without any sample preparation.

3. RESULTS AND DISCUSSION

Composites of acrylamide and TGDMA in 1:1 molar ratio were synthesized using 1 w% AIBN as initiator and 10-40 w% graphite as additive. Mixtures with higher graphite content could not be filled into the test tubes uniformly. The resistance of 5 mm thick disks were measured, and the resistivity \( R_s \) calculated. Composites with lower graphite content cannot be used in electrosynthesis experiments because high electrode resistance limits the cell current extending electrolysis time.

The porous composite structure is caused by the entrapment of gaseous byproducts (mainly nitrogen) formed in the decomposition of the initiator. The polymerization front is started on the top of the monomer mixture and travels down with a speed of 2-3 cm/min. In the reaction zone fast decomposition of the initiator produces high radical concentration which propagates fast formation of solid polymer matrix and the solidifying polymer traps in the gas bubbles.

Graphite additive changes the consistency of the monomer mixture from mobile (5%) to creamy (40%). Solid particles in small concentration facilitate bubble nucleation, but at high graphite content the heat conductivity of the monomer mixture is higher enhancing heat dissipation and causing front broadening providing more time for bubble fusion.

Number of pores were determined by digital image processing of photograps of cross sections of each composite using the Cprobe.
Pore size increases with increasing graphite content but the number of pores decreases. This results in decreasing surface area.

During electrosynthesis experiments different rates of hydrogen evolution have been observed at composite electrodes with various graphite content. This observation led us to measure the exchange current densities and the hydrogen overpotentials.

Exchange current densities were determined from Tafel-plot of overpotential – current data collected at 100 mV/s scanning speed. Increase of current density can be attributed to the decrease of resistivity with increasing graphite content. If more current flows through the electrode at a given voltage according to Ohm’s law, higher current densities are obtained.

Minimum decomposition overpotential of hydrogen was determined from overpotential-current data in the range of 0-6.25 mA/cm² current density.

Drossbach and Schulz [24] investigated the differences in hydrogen overpotential and exchange current density of various graphite samples having different pore size and density. They have found that both values are affected by the nature of the graphite.

Exchange current density and overpotential are directly related. The dependence is given by the Tafel equation:

\[ \eta = a + b \cdot \lg i \]

Where \( a \) and \( b \) are constants, and \( i \) is the exchange current density. Constant \( a \) is a measure of the catalytic power of the electrode surface, and \( b \) is related to the mechanism of the electrode reaction [25].

Experimental data and nonlinear curve fittings (prepared by using Origin 5.0) are plotted on figure 8. We obtained the curve named „fit 1” by applying the Tafel equation (parameters: \( a = 2,196, b = 0,231 \)) to all of the points. By considering only the first four points the second curve is obtained („fit 2”, \( a = 2,196, b = 0,231 \)). This curve runs over the experimental points which means that there is an effect lowering the hydrogen overvoltage on composites with higher graphite content.

By fitting the data with the following modified equation:

\[ y = a - cx + b \cdot \lg(x) \]

good accordance was found with the experimental values (\( a = 3,159, b = 0,491, c = 2,926 \)).

Incorporation of variable „c” can be justified by taking into consideration the differences in electrode surface area. The influence of electrode roughness (\( r \), which is the ratio of the real-
and the geometrical surface) on hydrogen overvoltage is a well-known phenomena.

Tafel equation extended with the roughness factor could be written as follows [25]:

$$\eta = a + b \cdot \log i - \log r$$

This approach points out the possible cause of difference from Tafel equation, but determination of Tafel constants and confirmation of the dependence on surface roughness can be done after the measurement of the real surface.

On graphite cathode, the reduction of acetophenone is masked by the reduction of water. This led us to perform small scale potentiostatic electrosynthesis experiments in order to gain information on the dependence of acetophenone reduction on electrode potential.

Between 2.5 and 3 V 1:1 alcohol/pinacol ratio have been found and at 4 V the alcohol have been the main product. The first peak can be related to the consecutive electron and proton uptake by acetophenone, resulting an intermediate radical, which is further reduced, or dimerize with an other radical. The second peak at 4 V points to an alternative reduction path resulting 1-phenylethanol, most likely with the participation of atomic hydrogen formed in the reduction of water. The formation of phenylethanol was interpreted in the literature with consecutive electron and proton uptake by the kethyl radical [10]. Because of the vigorous hydrogen evolution accompanying the electrolysis at 4V, it seems to be probable that the reaction of the kethyl radicals with hydrogen atoms becomes predominant at higher electrode potentials. As electrode potential is further increased hydrogen evolution accelerates and its mixing effect facilitates the transfer of radical intermediates to the bulk of the solution, where their coupling results the pinacol product and lowers the alcohol ratio. In our experiments the DL/meso ratio of the pinacol was independent from the electrode potential, it had a constant value of 0.3.

In the study of composite electrodes the conversion after one hour was too low for quantitation by HPLC, thus the conductivity of the electrolyte have been increased by using 0.3 M LiBr instead of 0.1 M.

By increasing graphite content the conductivity of the electrode and thus the rate of the reduction is higher.

The alcohol/pinacol ratio increases with electrode potential by every composite electrode, which is probably caused by the acceleration of the recombination of kethyl radicals with hydrogen atoms. Chemoselectivity increases with the graphite content, but it has a local maximum at 20-25 w%.

A possible cause of differences in chemoselectivity can be the unique structure of the composite, different from materials prepared by other incorporation techniques. The polymer matrix is formed in a free radical polymerization reaction, in which the growing polymer chain can react with a monomer, an other radical, or with the surface of a graphite particle. Dependence of resistivity on AA/TGDMA molar ratio at constant graphite content found by Judit Szalay [26] confirms this theory. The existence of polymer-graphite covalent bonds, and the role of polymer chains in the conductivity of the composites was proven by Tamás Károly [27]. Based on XPS results and molecular modelling he found electron density decrease on graphite, and increase on polymer carbons and oxygens. The study was extended to various acrylate cross-linkers, but the graphite content was kept constant at 25 w%. Considering the high reactivity of free radicals with electron rich partners, the extent of graphite-polymer interaction is likely to be governed by statistical effects, the probability of a growing chain gets close
enough to a graphite surface to form a covalent bond. This is likely to be dependent on the graphite / monomer volume ratio. We assume, that the electron transition between the electrode and the electrolyte takes place not only on the surface of graphite particles - as in the case of simple percolation conductor electrodes - but on the polymer surface also, which has different surface properties (polarity, hydrophilicity, electron density). Adsorption energy of each intermediates on different surfaces can be different, which leads to changes in chemoselectivity. 

Diastereoselectivity was found to be constant during electrosynthesis experiments, the meso/DL ratio was 0.25-0.3. This is in agreement with earlier findings [28], that the pinacolization takes place in the bulk of the solution, and the electrode material has no influence on meso/DL ratio.

The percentage current efficiency was calculated as the ratio of the charge required for the reduction of acetophenone and the measured charge passed through the cell. Current efficiency is determined by the electrode potential, and the electrode material. It is the highest at 2 V, and changes by a maximum curve in the function of graphite content. The cell resistance decreases with increasing graphite content, this leads to higher conversions, but the current efficiency decreases.

By decreasing graphite content the electric current is lower, and the rate of hydrogen evolution decreases in a greater extent than acetophenone reduction.

4. CONCLUSION

Frontal polymerization is a fast and convenient method for the preparation of composites with various composition. Graphite containing composites of acrylamide and TGDMA, prepared by this method are capable of use as electrodes in organic electrosyntheses. By changig the graphite ratio, the electrochemical properties of the electrodes can be controlled. Exchange current density of the reduction of water and minimum decomposition overpotential of hydrogen increases with graphite content. In the reduction of acetophenone not only the conversion an the current efficiency depends on the graphite content, but the chemoselectivity either. From the point of view of current efficiency the 15 w% graphite containing composite at -2 V (vs. SCE) is the best for the electroreduction, but the high resistance of this electrode extends electrolysis time. It is more practical to use an electrode with higher graphite content, but too high graphite content (40 w%) will increase the ratio of the phenylethanol, so faster electrolysis can lead to less pure product. The use of composite electrodes gives the possibility of tuning a new parameter in the optimization of organic electrosynthetic reaction conditions: the composition of the electrode. By incorporation of other additives – for example: metal powders, oxides or salts – the properties of the electrodes can further be modified.

REFERENCES