**Manganese Dioxide Graphite Composite Electrodes: Application to the Electroanalysis of Hydrogen Peroxide, Ascorbic Acid and Nitrite**

* Cathryn E. LANGLEY,* Biljana ŠLJUKIĆ,* Craig E. BANKS,** and Richard G. COMPTON*†

*Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom

**Now at Chemistry, School of Biomedical and Natural Sciences, Nottingham Trent University, Clifton Lane, Clifton, Nottingham, NG11 8NS, United Kingdom

The modification of carbon powder with manganese dioxide using a wet impregnation procedure with electrochemical characterisation of the modified powder is described. The process involves saturation of the carbon powder with manganese(II) nitrate followed by thermal treatment at ca. 773 K leading to formation of manganese(IV) oxide on the surface of the carbon powder. The construction of composite electrodes based on manganese dioxide modified carbon powder and epoxy resin is also described, including optimisation of the percentage of the modified carbon powder. Composite electrodes showed attractive performances for electroanalytical applications, proving to be suitable for the electrochemical detection of hydrogen peroxide, ascorbic acid and nitrite ions with limits of detection comparable to the detection limits achieved by other analytical techniques. The results obtained for detection of these analytes, together with composite electrodes flexible design and low cost offers potential application of composite electrodes in biosensors.

(Received September 5, 2006; Accepted October 24, 2006; Published February 10, 2007)

**Introduction**

Metal oxide electrodes possess some unique electrochemical properties compared to metal ones. Their advantages include enhancement of reaction rate due to redox couples of oxide species of two different states, as well as weak adsorption or complete exclusion of hydrogen species on an oxide surface. Among these catalysts, manganese oxides have attracted much interest due to their high catalytic activities with great potential as selective heterogeneous catalysts, adsorbents and battery materials. They have been used for a wide range of industrial catalytic applications: ozone decomposition, photocatalytic oxidation of organic pollutants and wastewater treatment, nitric oxide reduction, selective oxidations of carbon monoxide, alcohols, and others. Manganese dioxide is the preferred structure of manganese oxides for electrochemical applications due to its suitably high density and purity, electrochemical activity under a range of discharge conditions, as well as relatively inexpensive commercial production; it is by far the most common electrocatalytic cathode material used in primary batteries. However, unsupported manganese oxide catalysts suffer from very low surface areas.

Electrodes and immobilization matrices in biosensors are commonly made of different carbon based materials such as glassy carbon, graphite, carbon paste, carbon fibres, porous carbon and carbon spheres due to these materials’ wide potential window, rich surface chemistry, chemical inertness and low cost. The main drawback of carbon electrodes are slow electron transfer rates observed compared to those observed at metal electrodes but these can be improved by modification of the electrode surface. The modified electrodes show improved electrocatalytic responses with reduced overpotentials and increased voltammetric signals allowing low detection limits and high sensitivities.

Numerous biological and environmental substrates have been explored at carbon electrodes, among which the detection of hydrogen peroxide, ascorbic acid and nitrite ions have great significance. Hydrogen peroxide is extensively implicated in enzymatic reactions of interest and therefore sensitivity of electrodes towards reduction of hydrogen peroxide allows an effective low-potential amperometric determination of different analytes such as lactate, phenols, catechols and alcohols without using any metal or redox mediator. Yet, it is well known that the sensitivity of carbon towards hydrogen peroxide is low with large overpotentials required; however, literature reports show that the reduction of hydrogen peroxide is accelerated at CNTs with a significant lower overpotential of the hydrogen peroxide and enhanced reversibility of its voltammetry.

Ascorbic acid is widely used as an antioxidant in the food and drink industry. It is also important in several metabolic processes involving oxidation and reduction and is used in health care where it can increase high-density lipoprotein production, down-regulate cholesterol and lower blood sugar and insulin requirements. Hence, the detection of ascorbic acid is of great importance in food and pharmaceutical industry. However, it is almost impossible to determine ascorbic acid by direct electrochemical oxidation on many conventional...
electrodes due to large overpotentials and electrode fouling by the oxidation products.\textsuperscript{24,25} The potential application of electrodes modified with different catalysts has been studied for ascorbic acid determination.

Nitrites are used extensively as additives in food, agriculture preservation and as corrosion inhibitors\textsuperscript{26} and are significant contaminants in food products, water and environment. The nitrite ions can combine with blood pigments to produce metha-hemoglobin in which oxygen is no longer available to the tissues. Also they may interact in the stomach with amines and amides to produce highly carcinogenic N-nitrosamine compounds, with fatal dose of nitrite by ingestion being between 8.7 - 28.3 μM.\textsuperscript{27,28} As a result of their potential toxicity, nitrite determination is important for environment and for public health. Although nitrites are electroactive at carbon electrodes, their oxidation requires undesirably high overvoltages.\textsuperscript{29} Consequently the voltammetric determination of nitrite suffers from interference of other readily oxidizable compounds. In order to improve the selectivity of the determination of nitrite, the operating potentials should be efficiently lowered which can be achieved by modifying suitable electrocatalysts on the surface of carbon electrodes.

In this paper we describe a simple method for the modification of carbon powder with manganese dioxide via a wet impregnation procedure with electrochemical characterisation of the modified powder. Construction of composite electrodes based on manganese dioxide modified carbon powder and their application for hydrogen peroxide, ascorbic acid and nitrite ions sensing is also presented.

**Experimental**

**Reagents and chemicals**

All chemicals and reagents used in this work were of the analytical grade and used as received without further purification. These were: manganese(II) nitrate (Alfa Aesar, 99.98%), manganese dioxide (Sigma), hydrogen peroxide (Sigma, 30% w/w solution), ascorbic acid (Aldrich, 99+%), sodium nitrite (Analar), perchloric acid (Aldrich, 70% w/w solution, redistilled, 99.999%) and sodium perchlorate (Aldrich, 99%).

For the electrode fabrication, carbon powder (Aldrich, 99.999%) and sodium perchlorate (Aldrich, 99+%), copper wire. The electrodes were subsequently dried at 40˚C for 30 min and then placed in a glass tube of 6 mm inner diameter up to 6 mm depth. The electrical contact was completed using a copper wire. The electrodes were subsequently dried at 40˚C for 60 h. Before each use, the surface of the working electrode was renewed, first polishing using abrasive paper and then polishing to a mirror-like finish with 1.0 and 0.3 μm alumina slurries (Buehler). For comparative purposes, carbon powder and composite electrodes were also prepared by the same procedure.

**Apparatus**

Voltammetric measurements were carried out on a μ-Autolab (ECO-Chemie, Utrecht, The Netherlands) potentiostat. All measurements were conducted in a thermostatted (22˚C) three-electrode cell. The working electrode was made of a manganese dioxide modified carbon powder and epoxy resin composite (see below for construction details). For comparison purposes, electrode based on carbon powder and epoxy resin composite was also prepared. The counter electrode was a platinum electrode (3 mm diameter), with a saturated calomel electrode (SCE, Radiometer, Copenhagen, Denmark) completing the circuit. Before commencing experiments, nitrogen (BOC, Guildford, Surrey, UK) bubbling was used for the deaeration of solutions.

**Procedures**

Different electrochemical methods were employed for determination of hydrogen peroxide, ascorbic acid and nitrite ion concentration: chronoamperometry (CA), cyclic voltammetry (CV) and linear sweep voltammetry (LSV). In all experiments, measurements of analyte concentrations were performed in a three-electrode electrochemical cell of 15 cm³ volume at room temperature. The electrochemical determination of analyte concentrations was performed via the standard addition protocol. The procedure involves spiking the analyte solution of unknown concentration with analyte solution of known concentration; the initial analyte concentration can then be determined by reading the peak current increase with each addition.

**Modification of carbon powder**

The modification of carbon powder with manganese dioxide was carried out by a wet impregnation procedure. The carbon powder was modified by stirring 1 g of carbon powder for 1 h in 25 cm³ of 5 M manganese(II) nitrate aqueous solution. The manganese nitrate-carbon powder composite was separated from the solution by filtration and left to dry at room temperature. Subsequently, the sample was kept at 793 K over night, resulting in the transformation of manganese(II) nitrate into manganese(IV) oxide as verified by electrochemical characterisation of modified carbon powder (see below).

**Preparation of the working electrode**

Composite working electrodes were made of manganese dioxide modified carbon powder, unmodified carbon powder and epoxy resin. MnO₂-CP-E composite electrodes were prepared by first hand-mixing epoxy resin and hardener in a 20:3 weight ratio. This was next blended with a mixture of manganese dioxide modified carbon powder (10 w%) and unmodified carbon powder (90 w%), with powder to resin ratio of 1:3. The resulting paste was mixed in an ultrasonic bath for 30 min and then placed in a glass tube of 6 mm inner diameter up to 6 mm depth. The electrical contact was completed using a copper wire. The electrodes were subsequently dried at 40˚C for 60 h. Before each use, the surface of the working electrode was renewed, first polishing using abrasive paper and then polishing to a mirror-like finish with 1.0 and 0.3 μm alumina slurries (Buehler). For comparative purposes, carbon powder epoxy composite, CP-E, electrodes were also prepared by the same procedure.

**Results and Discussion**

**Characterisation of the manganese dioxide modified graphite powder and composite electrodes**

First performed was the electrochemical characterisation of the carbon powder modified with manganese dioxide and composite electrodes based on the manganese dioxide modified carbon powder and epoxy composite, MnO₂-CP-E.

Carbon powder modified from manganese(II) nitrate solution via wet impregnation procedure was characterised using cathodic stripping voltammetry (CSV). The modified carbon powder was abrasively attached to basal plane pyrolytic graphite, BPPG, electrode by gently rubbing the electrode surface on a fine abrasive paper containing manganese dioxide modified carbon powder. A BPPG electrode surface was prepared for modification with cellotape (TM).\textsuperscript{30} This involves first polishing the electrode surface on carbon paper. Next cellotape was pressed on the clean electrode surface and removed along with several surface layers of graphite.\textsuperscript{30} This process was repeated many times before
modification. The electrode was finally cleaned in acetone to remove any adhesive.

Stripping voltammograms of modified BPPG electrode were run in pH 1 HNO₃ + KNO₃ solution at scan rate of 100 mV s⁻¹. The cathodic stripping peak of manganese dioxide from modified carbon powder attached to BPPG electrode, Eq. (1), could be observed at ca. +0.36 V vs. SCE, Fig. 1A.

\[ \text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad (1) \]

For comparison purposes, BPPG electrode was abrasively modified with commercially available manganese dioxide and CSV run in the same pH 1 solution, Fig. 1B. The stripping peak of manganese dioxide abrasively attached to BPPG electrode appears at the same potential as the peak obtained for carbon powder modified BPPG electrode, evidencing existence of manganese(IV) oxide on carbon powder modified via the described wet impregnation procedure.

Next, the effect of the amount of manganese dioxide modified carbon powder on the composite electrode electrochemical behavior was explored. Composite electrodes with various percentages of manganese dioxide modified carbon powder were made by adding unmodified carbon powder. It was found that increasing the amount of manganese dioxide modified carbon powder, the electron transfer at the MnO₂-CP-E composite electrode becomes apparently slower with the peak-to-peak separation increasing, Fig. 2, due to the increase of resistance through the electrode resulting in decreased electrode kinetics. The resistance of the composite electrode with 10 w% of manganese dioxide modified carbon powder and 90 w% of unmodified carbon powder was found to be 4.47 kΩ and the electrodes of this composition were used throughout all further experiments.

**Hydrogen peroxide detection**

Next the application of the manganese dioxide modified carbon powder epoxy composite electrodes, MnO₂-CP-E, for the determination of hydrogen peroxide in aqueous solutions using cyclic voltammetry and chronoamperometry was examined. First, series of cyclic voltammograms of MnO₂-CP-E composite electrode were run between 0 and +1.0 V vs. SCE in pH 7.4 phosphate buffer. pH 7.4 was selected since it has been reported to be the optimum pH value for hydrogen peroxide detection via electrochemical methods using multi-walled carbon nanotube modified glassy carbon electrodes. ³¹ This pH offers the potential application for the MnO₂-CP-E composite electrodes in biosensors operating in biological media/conditions. No peak is observed in the pH 7.4 phosphate buffer in the absence of hydrogen peroxide. Following addition of a fixed amount of hydrogen peroxide (5 mM), a distinct peak corresponding to the electrochemical oxidation of hydrogen peroxide could be observed at ca. +0.70 V vs. SCE, Fig. 3. For comparison, cyclic voltammogram of carbon powder epoxy composite electrode was also run under the same conditions and only an indistinct peak was observed.

Subsequently, the amperometric response of MnO₂-CP-E composite electrode was explored under conditions where the potential was held at +0.70 V vs. SCE. Figure 4 depicts the current-time response from the additions of hydrogen peroxide to a pH 7.4 phosphate buffer. Successive additions from 0.25 to 3 mM in 90 s intervals produced a well defined linear response. From this graph, a limit of detection was calculated based on 3 sigma method:

\[ \text{LOD} = 3\bar{\delta}b \quad (2) \]

where \(\bar{\delta}\) is the standard deviation of the y-coordinates from the line of best fit and \(b\) the slope of the same line. The value of 1.4 μM for limit of detection of hydrogen peroxide using MnO₂-CP-E composite electrode was calculated. The detection limit for hydrogen peroxide obtained from chronoamperometry data.
using manganese dioxide modified carbon powder epoxy composite electrode is comparable to the limits of detection attainable with existing methods that range from 0.12 to 10.3 μM, Table 1.

**Ascorbic acid detection**

Next the potential application of MnO2-CP-E composite electrodes for ascorbic acid sensing was investigated using cyclic voltammetry. A cyclic voltammogram of MnO2-CP-E composite electrode was run in 0.5 mM solution of ascorbic acid in pH 7.2 phosphate buffer at scan rate of 50 mV s⁻¹ with a distinct peak observed at ca. +0.225 V vs. SCE. No peak was observed if the CV of MnO2-CP-E composite electrodes was run in pH 7.2 phosphate buffer with no ascorbic acid added. pH 7.2 was used for determination of ascorbic acid since it reflects real sample conditions and most of the studies reported in the literature are carried out in this pH.32–34 The oxidation current was found to increase with increasing the concentration of ascorbic acid; Fig. 5 shows the voltammetric responses of the MnO2-CP-E composite electrodes to the additions of ascorbic acid into a pH 7.2 phosphate buffer solution. Distinct voltammetric peaks are obtained for concentrations as low as 250 μM ascorbic acid. The calibration curve exhibited a linear range up to 2.5 mM with a limit of detection (based on 3σ) for ascorbic acid of 0.4 μM. This detection limit is lower or comparable to the ones obtained with existing methodologies35–38 that range from 0.08 to 71 μM as shown in Table 2.

**Nitrite ions detection**

Next, the manganese dioxide modified carbon powder epoxy composite electrode was tested for the detection of nitrite ions. Cyclic voltammograms of MnO2-CP-E composite electrode were initially run in 10 mM sodium nitrite aqueous solution, with a distinct peak observed at ca. +0.95 V vs. SCE. No peak was observed in the absence of nitrite. Subsequently, 250 μM additions of nitrite were added into 1 mM HClO4 + 1 M NaClO4 solution where noticeable increases in the peak current were observed after each addition, Fig. 6. Distinct current raise is obtained for concentrations as low as 200 μM sodium nitrite. The peak current values showed a strong linear correlation with nitrite concentration with a limit of detection (based on 3σ) for nitrite of 1.2 μM. Note that this detection limit is lower or comparable to the ones obtained with existing methodologies39–44 and other techniques45–47 shown in Table 3. This method has a

### Table 1 Comparison of performances of different electrochemical sensors for hydrogen peroxide

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Linear range/μM</th>
<th>Detection limit/μM</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO2-CPE in pH 8.50⁶</td>
<td>0.3 – 3631</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Nanostructured MnO2-CPE in pH 7.4⁴⁷</td>
<td>100 – 690</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>VZrO2-graphite/polyester composite electrode⁸ at pH 10⁹⁷</td>
<td>5 – 400</td>
<td>0.9</td>
<td>170</td>
</tr>
<tr>
<td>Fe₃O₄-GC⁹ rotating disk electrode in pH 3 (1) and pH 7 (2)⁵²</td>
<td>Up to 4000(1)</td>
<td>7.6(1)</td>
<td>16.8(1)</td>
</tr>
<tr>
<td>MnHCF-Al electrode in pH 6.5⁵⁶</td>
<td>5000(2)</td>
<td>7.4(2)</td>
<td>9.6(2)</td>
</tr>
<tr>
<td>Myb/MWCNTs-GCE¹⁰ in pH 4⁵⁸</td>
<td>0 – 330</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>HRP/MWCNTs/chitosan-GCE in pH 6.9⁹⁶</td>
<td>16.7 – 740</td>
<td>10.3</td>
<td>4.995</td>
</tr>
<tr>
<td>Sol-gel/hydrogel composite film-GCE in pH 7.5⁵⁵</td>
<td>Up to 3400</td>
<td>0.5</td>
<td>15</td>
</tr>
<tr>
<td>Ag nanoparticle-GCE in pH 7.4⁵⁷</td>
<td>5 – 40</td>
<td>2.0</td>
<td>1.40 × 10⁻³</td>
</tr>
<tr>
<td>Fe₂O₃-graphite-epoxy composite electrode in pH 7.4⁴⁷</td>
<td>250 – 5000</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>MnO2-CP-E electrode in pH 7.4⁴⁸</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. CPE: carbon paste electrode.
b. VZrO₂: vanadium doped zirconias.
c. GCE: glassy carbon electrode.
d. Myb: myoglobin.
e. MWCNT: multi wall carbon nanotube.
f. HRP: horseradish peroxidase.
g. MnO2-CP-E: manganese dioxide modified carbon powder epoxy composite electrode.

---

**Fig. 4** Amperometric response observed at the MnO2-CP-E composite electrode from 0.25 mM additions of hydrogen peroxide to a pH 7.4 phosphate buffer solution at operating potential of +0.70 V vs. SCE with standard addition plot (insert).

**Fig. 5** Cyclic voltammograms for the oxidation of ascorbic acid at MnO2-CP-E composite electrode in pH 7.2 phosphate buffer increasing the ascorbic acid concentration at scan rate of 50 mV s⁻¹ with standard addition plot (insert).
potential application to control the concentration of nitrite in drinking water where the maximum allowed nitrite level is 2.7 μM. 48

Conclusions

Novel manganese dioxide modified carbon powder epoxy composite electrodes have been fabricated using carbon powder modified with manganese dioxide via a wet impregnation procedure. The composite electrodes showed good performances and potential application in electroanalysis with sensitivity and selectivity for detection of different analytes. Hydrogen peroxide, ascorbic acid and nitrite were all detected at limit of detections comparable to or better than existing methods. Due to the simplicity and cheapness of the preparation procedures with flexibility in design and the fast routine determination, the composite electrodes can be used for the direct electroanalytical determination of these and other important analytes. In addition, these composite electrodes may have potential applications in biosensing.

Acknowledgements

B. S. thanks the Clarendon Fund for partial funding.

References


