

Electrocatalytic Reduction of Oxygen at Au Nanoparticles–Manganese Oxide Nanoparticle Binary Catalysts

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The electrocatalytic reduction of molecular oxygen (O_2) has been performed in O_2 -saturated 0.5 M KOH solution at binary catalysts of Au nanoparticles and manganese oxide (MnOx) nanoparticles electrodeposited onto glassy carbon (GC) electrodes. Cyclic voltammetric (CV) and rotating ring-disk electrode (RRDE) techniques have been utilized in this study. CV measurements showed that the electrochemically deposited MnOx nanoparticles have a good catalytic activity toward the disproportionation of hydrogen peroxide (HO₂⁻ in alkaline media) to water and O_2 . A significant positive shift of the peak potential of the oxygen reduction reaction (ORR) was observed upon loading Au nanoparticles onto the GC substrate. The combined use of MnOx and Au nanoparticles resulted in the occurrence of the ORR at a potential close to that obtained at Pt electrodes, supporting an apparent four-electron reduction pathway as revealed from the RRDE voltammetric results. The current study proposed a novel binary catalyst system (composed of metal/metal oxide nanoparticles) as a very promising candidate to replace the costly Pt-based electrocatalysts in alkaline air electrodes.

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A four-electron reduction of oxygen (to water) at a reasonably low cathodic overpotential is a major goal in the development of non-Pt-based electrocatalysts.¹⁻⁸ This reaction has a vital role in energy conversion technologies, such as metal air batteries and fuel cells.^{2,9-11} Thus, numerous efforts have been paid to the search for cheaper materials with excellent electrocatalytic activity toward the oxygen reduction reaction (ORR) to replace the costly Pt-based electrocatalysts. Nanoparticle-based electrocatalysts stand as one of the most promising candidates for diverse applications.¹²⁻²² Recently, Au(100)-like, gold nanoparticle-based electrocatalysts have been prepared by proper adjustment of the electrodeposition conditions.^{23,24} Yet, a direct four-electron reduction of oxygen is not fully verified at these electrodes, probably due to the contribution of the two-electron reduction pathway of O_2 (to hydrogen peroxide) at other facets of the Au nanoparticles simultaneously deposited (albeit at low ratios) [i.e., Au(111) and Au(110)].^{23,24} Thus, in a trial to overcome this problem, manganese oxide (MnOx) nanoparticles were electrodeposited onto the Au nanoparticle-electrodeposited glassy carbon (GC) (nano-Au/GC) electrodes to enhance the catalytic disproportionation of hydrogen peroxide electrogenerated at these coexisting facets. This was done utilizing the dual benefit of both materials, i.e., the positive potential shift of the ORR caused by the electrodeposition of Au nanoparticles and the increase of the current caused by the MnOx. Thus, an apparent four-electron reduction of O_2 would occur at a potential closer (or more positive) to that of the Pt electrode.

This study explores the effect of the sequential electrodeposition of Au and MnOx nanoparticles onto the GC electrodes and the impact of the electrodeposition order of both species on the reduction pathway of molecular oxygen in alkaline medium of 0.5 M KOH saturated with oxygen gas.

Experimental

Cyclic voltammetric (CV) measurements were performed in a conventional two-compartment three-electrode Pyrex glass cell using a computer-controlled BAS 100 B/W electrochemical analyzer. The working electrode was a GC rod ($\phi = 3.0 \text{ mm}$ diam) sealed in a Teflon jacket leaving an exposed geometric surface area of 0.07 cm². A spiral Pt wire and an Ag/AgCl/KCl (sat.) were the counter and the reference electrodes, respectively. Steady-state voltammograms were obtained at a GC disk ($\phi = 3.0 \text{ mm}$)–Pt ring

electrode using a rotary system from Nikko Keisoku (Japan) coupled with an ALS/chi 832A electrochemical analyzer bipotentiostat (USA). The working electrode compartment was 200 cm³ to eliminate any possible change of the O₂ concentration during the measurements. Prior to each experiment, O2 gas was bubbled directly into the cell for 30 min to obtain an O₂-saturated 0.5 M KOH solution; during every measurement O2 gas was flushed over the cell solution. GC electrodes were mechanically polished first with no. 2000 emery paper and then with aqueous slurries of successively finer alumina powder (down to $0.06 \ \mu m$) with the help of a polishing microcloth, and then sonicated for 10 min in Milli-Q water. Au nanoparticles were electrodeposited on the thus-prepared GC electrodes (nano-Au/GC) from acidic solution of 0.5 M H₂SO₄ containing 1.0 mM Na[AuCl₄]. A 300 s potential step electrolysis from 1.1 to 0 V vs Ag/AgCl/KCl(sat) was utilized to perform the electrodeposition of the Au nanoparticles. Manganese oxide (MnOx) nanoparticles were electrodeposited onto the GC (or nano-Au/GC) electrodes from a solution containing 0.1 M Na₂SO₄ + 0.1 M Mn(CH₃COO)₂ via cycling the potential between 0.0 and 0.4 V vs Ag/AgCl/KCl(sat) for 25 cycles at 20 mV s⁻¹.²⁵ Selfassembled monolayers (SAMs) of a thiol compound (typically cysteine) were formed on the different Au/MnOx nanoparticleelectrodeposited GC electrodes by immersion into an aqueous solution of 1.0 mM cysteine for 10 min.

The collection efficiency, N, of the rotating ring-disk electrode (RRDE) was measured using 1.0 mM K_3 [Fe(CN)₆] in 0.5 M KCl, and a value of 0.38 ± 0.02 was obtained for the GC disk-Pt ring RRDE, while a value of 0.42 ± 0.02 was obtained for the Pt disk-Pt ring RRDE. All current densities were calculated on the basis of the geometric surface area of the electrodes (i.e., 0.07 cm^2). All the measurements were performed at room temperature ($25 \pm 1^{\circ}$ C). All chemicals used in this investigation were of analytical grade and were used without further purification. X-ray diffraction (XRD) measurements were performed on a Philips PW 1700 powder X-ray diffractometer using Cu K α_1 radiation ($\lambda = 1.54056$ Å) with a Ni filter working at 40 kV and 30 mA. Scanning electron microscopy (SEM) analysis of the Au (and/or MnOx) nanoparticles electrodeposited onto the GC electrodes was carried out using an JSM-T220 scanning electron microscope (JEOL Optical Laboratory, Japan) at an acceleration voltage of 20 kV and a working distance of 4-5 mm.

Results and Discussion

Characterization of the MnOx/Au nanoparticles electrodeposited GC electrodes.— Measurements of the characteristic I–E curves.— Figure 1 shows the characteristic current–potential I–E curves obtained at (a) bare GC, (b) nano-MnOx/GC, (c) nano-Au/GC, (d)

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Figure 1. CVs obtained for (a) bare GC, (b) nano-MnOx/GC, (c) nano-Au/GC, (d) nano-MnOx/nano-Au/GC, and (e) nano-Au/nano-MnOx/GC electrodes ($\varphi = 3.0 \text{ mm}$) in N₂-saturated 0.5 M H₂SO₄. Potential scan rate 100 mV s⁻¹. MnOx nanoparticles were electrodeposited from 0.1 M Na₂SO₄ + 0.1 Mn(CH₃COO)₂ by applying 25 potential cycles between 0 and 0.4 V vs Ag/AgCl/KCl(sat) at 20 mV s⁻¹. The Au nanoparticles were electrodeposited from 0.5 M H₂SO₄ containing 1.0 mM Na[AuCl₄] by applying a 300 s potential step electrolysis from 1.1 to 0 V vs Ag/AgCl/KCl(sat).

nano-MnOx/nano-Au/GC, and (e) nano-Au/nano-MnOx/GC electrodes in $N_2\mbox{-saturated}$ 0.5 M $H_2SO_4.$ MnOx nanoparticles were electrodeposited onto the GC (nano-MnOx/GC) electrodes from aqueous solution of 0.1 M Na₂SO₄ and 0.1 M Mn(CH₃COO)₂ by applying 25 potential cycles between 0 and 0.4 V vs Ag/AgCl/KCl(sat) at 20 mV s⁻¹. Au nanoparticles were electrodeposited onto the GC (or the nano-MnOx/GC) electrodes from aqueous acidic solution of 0.5 M H₂SO₄ containing 1.0 mM Na[AuCl₄] by applying a 300 s potential step electrolysis from 1.1 to 0 V vs Ag/AgCl/KCl(sat). For the electrodes employed in the measurements of curves d and e of Fig. 1, the electrodeposition of MnOx and Au nanoparticles onto the GC electrodes were done as two separate steps with different sequence, i.e., for case d (i.e., nano-MnOx/nano-Au/GC) Au nanoparticles were first electrodeposited onto the bare GC electrodes followed by the electrodeposition of MnOx and vice versa for case e. Inspection of this figure reveals the following: (i) the electrodeposition of MnOx onto the nano-Au/GC electrodes seems to have a negligible influence on the accessible surface area of the Au nanoparticles (compare curves c and d), (ii) a smaller amount of Au has been electrodeposited onto the GC electrodes with a predeposited nano-MnOx (compare curves c and e), and (iii) the nano-MnOx possesses some sort of electrochemical activity as revealed from the broad (rather small) reduction peak located at ca. +1.1 V (see curve b of Fig. 1). The real surface areas



Figure 2. CVs obtained at (1) 1st and (2) 2nd potential scans for the reductive desorption of cysteine SAMs formed at (a) nano-Au/GC, (b) nano-MnOx/nano-Au/GC, and (c) nano-Au/nano-MnOx/GC electrodes (ϕ = 3.0 mm) measured in N₂-saturated 0.5 M KOH. Potential scan rate 50 mV s⁻¹. The electrodeposition conditions used for MnOx and Au nanoparticles were the same as in Fig. 1.

of the Au nanoparticles electrodeposited onto the GC (or the nano-MnOx/GC) electrodes were estimated by calculating the amount of charge consumed during the reduction peak of the Au surface oxide monolayer [located at ca. +0.9 V vs Ag/AgCl/KCl(sat)] using a reported value of 400 μC cm $^{-2}.^{26}$ Table I summarizes the loading characteristics of the Au nanoparticles electrodeposited onto different electrodes.

Measurements of the reductive desorption patterns of cysteine SAM formed on the different nano-MnOx/nano-Au/GC electrodes.— It has been reported that the electrodeposited Au nanoparticles are composed mainly of three low-index crystallographic orientations, i.e., Au(111), Au(100), and Au(110) in a relative ratio depending on the electrodeposition conditions.^{23,27,28} The relative ratios of the different single-crystalline domains of the Au nanoparticles electrodeposited onto different electrodes were assessed by the measurements of the reductive desorption patterns of a SAM of a thiol compound (typically cysteine) formed at the different nano-Au(and/or nano-MnOx)/GC electrodes. Figure 2 shows the CVs of the reductive desorption of cysteine SAMs formed on (a) nano-Au/ GC, (b) nano-MnOx/nano-Au/GC and (c) nano-MnOx/nano-Au/GC electrodes in N2-saturated 0.5 M KOH solution at a scan rate of 50 mV s. The multiple reduction peaks located at ca. -0.7, -1.0, and -1.1 V were assigned, respectively, to the reductive desorption of the chemisorbed cysteine molecules from the Au(111), Au(100), and Au(110) single-crystalline facet domains constituting the Au nanoparticles.^{23,27,28} The relative ratio of the peak current intensities is reasonably proportional to the relative ratio of the low-index

Table I. Relative ratios of the Au(111) and Au(100) + Au(110), total thiol (cysteine) surface coverage (I), the amount of Au nanoparticles deposited (M_{Au}), and the specific surface area (S) of the different nano-Au(and/or nano-MnOx) GC electrodes (same notation as Fig. 1).

Electrode	Au(111) (%)	Au(100) + Au(110) (%)	Γ (mol cm ⁻²)	${M_{ m Au}} \ ({ m g})$	$\frac{S}{(\mathrm{cm}^2\mathrm{g}^{-1})}$
Nano-Au/GC	26.7	73.3	1.2×10^{-9}	1.81×10^{-6}	$4.8 imes 10^4$
Nano-MnOx/nano-Au/GC	23.1	76.9	1.3×0^{-9}	1.81×10^{-6}	$5.8 imes 10^4$
Nano-Au/nano-MnOx/GC	19.1	80.9	7.1×10^{-10}	1.56×10^{-6}	4.2×10^{4}



Figure 3. SEM images for the (a) nano-MnOx/GC, (b) nano-Au/GC, (c) nano-Au/ nano-MnOx/GC, and (d) nano-MnOx/ nano-Au/GC electrodes. The electrodeposition conditions used for MnOx and Au nanoparticles were the same as in Fig. 1.

single-crystalline orientation domains constituting the surface of the polycrystalline Au nanoparticles. Table I summarizes the relative ratios of the Au(111) and Au(100) + Au(110) of the different nano-Au(MnOx)/GC electrodes as estimated by integrating the charge consumed at ca. -0.7 and in the region of -1.0 to -1.1 V, respectively. Obviously, the amount of cysteine is proportional to the accessible area of the Au nanoparticles. A significant decrease of the two peaks located at ca. -0.7 and -1.0 to -1.1 V in the case of nano-MnOx/nano-Au/GC electrode (case c) is associated with the small mount of Au electrodeposited, but a relative enrichment of the Au(100) + Au(110) has been observed. While the electrodeposition of MnOx onto the nano-Au/GC electrodes (case b) does not affect the relative ratio of their single-crystalline facet domains (compare a and b).

SEM and XRD characterization of the different Au/MnOx nanoparticles electrodeposited onto GC electrodes.- Figure 3 a-d shows the SEM micrographs obtained for (a) nano-MnOx/GC, (b) nano-Au/GC, (c) nano-Au/nano-MnOx/GC, and (d) nano-MnOx/ nano-Au/GC electrodes. The MnOx was electrodeposited in a porous texture composed of nanorods onto the GC electrode (Fig. 3a). This texture homogeneously covers the entire surface of the GC electrode in a rather porous texture form, which enables the accessibility of the solution species to the underlying GC substrate through nano channels across the MnOx nanotexture. The beneficial electrocatalytic effect of this structure is demonstrated later toward the ORR at this electrode. Au nanoparticles of round-shaped plumbs were electrodeposited onto the bare GC electrode (Fig. 3b) having particle size in the range of 10 to 100 nm. While, when electrodeposited onto GC electrode with a predeposition of MnOx (i.e., nano-MnOx/GC), Au nanoparticles with a different aggregate morphology and a larger particle size ranging from 50 to 200 nm were obtained with disappearance of the nanorods texture of the predeposited MnOx (Fig. 3c). Interestingly, the electrodeposition of MnOx onto the nano-Au/GC electrodes resulted in the formation of the nanorod texture onto the round-shaped Au nanoparticles (Fig. 3d). That is, the MnOx electrodeposition takes place at the Au nanoparticles rather than at the bare portion of the GC electrode. The following section demonstrates the electrocatalytic activity of the individual electrodes toward the ORR in alkaline medium. Figure 4 shows the XRD patterns measured for the same electrodes shown in Fig. 3. The highly amorphous nature of the GC substrates disabled the monitoring of the different peaks of both species (i.e., nano-Au and nano-MnOx). Only the peak due to the Au(111) facet of the Au nanoparticles could be observed (at 20 of ca. 38.5°) with different XRD peak intensities. The decrease of the intensity of this peak upon the loading of nano-MnOx indicates the occurrence of the electrodeposition onto the nano-Au rather than on the bare portion of the GC substrate (compare curves c and d), being consistent with the visual observation of the SEM image (Fig. 3d). The diffraction peaks located at 20 values of ca. 26, 43, and 78° are attributed to the (111), (011), and (110) planes of the carbon substrate, respectively.²⁹

Oxygen reduction at the different nano-MnOx/nano-Au/GC electrodes.— Cyclic voltammetry.— Figure 5 shows the CVs for the ORR measured at (a) bare GC, (b) nano-MnOx/GC, (c) nano-Au/ GC, (d) nano-MnOx/nano-Au/GC, (e) nano-MnOx/nano-Au/GC, (f) nano-Au/nano-MnOx/nano-Au/GC electrodes in O₂-saturated 0.5 M KOH. This figure reflects many interesting points:

1. A single reduction wave was observed for the ORR at all the electrodes in the employed potential window, the peak potential of which is inherently dependent on the nature of the electrodeposited species and the deposition sequence.

2. Electrodeposition of nano-MnOx onto the GC electrode (curve b) resulted in the occurrence of the ORR at the same potential [at ca. -0.36 V vs Ag/AgCl/KCl(sat)] as that obtained at the bare GC electrode (curve a) with an enlarged peak current (about 1.3 times).

3. The electrodeposition of Au nanoparticles onto the bare GC electrode (curve c) resulted in a significant positive shift of the ORR peak potential [at ca. -0.16 V vs Ag/AgCl/KCl(sat)] with about 1.8 times higher peak current compared to that obtained at the bare GC electrode (curve a).

4. The ORR takes place at almost the same potential at the nano-Au/GC (curve c) and nano-Au/nano-MnOx/GC (curve d) electrodes



Figure 4. XRD patterns for the (a) nano-MnOx/GC, (b) nano-Au/nano-MnOx/GC, (c) nano-Au/GC, and (d) nano-MnOx/nano-Au/GC electrodes. The electrodeposition conditions used for MnOx and Au nanoparticles were the same as in Fig. 1.

(at ca. -0.16 V), but the latter electrode, advantageously, showed a peak current of about double intensity compared to that obtained at the bare GC electrode (curve a).

5. Inversing the order of electrodeposition of Au nanoparticles and MnOx nanoparticles, i.e., the electrodeposition of MnOx onto the nano-Au/GC electrode (i.e., nano-MnOx/nano-Au/GC electrode, curve e), resulted in a rather broad reduction peak of the ORR located at -0.36 V while retaining a peak current ratio about 1.3 times higher than that supported by the bare GC electrode (curve a).

6. Interestingly, the electrodeposition of Au nanoparticles onto the nano-MnOx/nano-Au/GC electrode (curve f) resulted in a most pronounced positive shift of the peak potential of the ORR (at ca. -0.12 V) among the examined electrodes with a double peak current intensity compared to the bare GC electrode (curve a).

The above results point out the importance of the design of the electrocatalyst in terms of the nature of the electrodeposited species and the sequence of electrodeposition. It is well-known that the ORR proceeds via a two-electron reduction pathway (to hydrogen peroxide, HO_2^- in alkaline medium) at the bare GC electrodes in alkaline media in this potential window,²⁴ which can be represented as

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$$
[1]

The increase of peak current upon loading the nano-MnOx onto the GC electrode is attributed to the catalytic disproportionation activity of manganese oxide. Thus, the MnOx-assisted decomposition of the electrogenerated hydrogen peroxide (HO₂⁻) to water and molecular oxygen takes place at this electrode

$$HO_2^- \rightarrow O_2 + OH^-$$
 [2]

The produced oxygen molecules (from Reaction 2) are reduced again to HO_2^- , leading to the observed high peak current intensity at this electrode. The electrodeposited Au nanoparticles enhanced the electrocatalytic activity of the electrode via the positive shift of the ORR potential. The combined use of both MnOx and Au nanoparticles (via electrodeposition onto the bare GC electrode) resulted in the above-mentioned behavior with different enlargements



Figure 5. CVs for the ORR at (a) bare GC, (b) nano-MnOx/GC, (c) nano-Au/GC, (d) nano-Au/nano-MnOx/GC, (e) nano-MnOx/nano-Au/GC, and (f) nano-Au/nano-MnOx/nano-Au/GC electrodes ($\phi = 3.0 \text{ mm}$) in O₂-saturated, 0.5 M KOH. Potential scan rate 100 mVs⁻¹. The electrodeposition conditions used for MnOx and Au nanoparticles were the same as in Fig. 1.

of the ORR peak current. The double peak current obtained at some electrodes (e.g., curves c, d, and f in Fig. 5) compared to that obtained at the bare GC electrode (curve a, Fig. 5) indicates the approach of the ORR to an apparent four-electron reduction pathway (to OH^{-}).

At this stage the reduction pathway of the ORR is not fully addressed. Consequently, in order to give a more detailed and realistic interpretation of the origin of the double peak current obtained, a steady-state hydrodynamic voltammetry (using RRDE) is applied hereafter, because it is suitable for diagnosing the pathway of the oxygen reaction at the different disk electrodes. This technique provides a real-time monitoring of the reduction product intermediates (i.e., hydrogen peroxide, HO_2^-) electrogenerated during the electrochemical reduction of oxygen at the different nano-Au(MnOx)/GC electrodes.

Steady-state hydrodynamic voltammetry.— Figure 6a-e shows the steady-state hydrodynamic voltammograms (RRDE) for the ORR at (a) bare GC disk, and (b) nano-MnOx/GC disk, (c) nano-Au/GC disk, (d) nano-MnOx/nano-Au/GC disk, and (e) nano-Au/ nano-MnOx/GC disk ($\phi = 3.0 \text{ mm}$) (I_D , bottom set of curves of each plot)–Pt ring electrodes (RRDE) in O₂-saturated 0.5 M KOH at different rotation rates. The Pt ring was potentiostatted at +0.5 V vs Ag/AgCl/KCl(sat). The top curves of each plot represent the corresponding Pt ring current (I_R) (due to the oxidation of HO₂⁻ generated at the disk electrode). The electrodeposition of Au (and/or) MnOx nanoparticles was performed as described in the Experimental section. Inspection of the different hydrodynamic voltammograms measured for the ORR at the different nano-Au (and/or nano-MnOx)/GC disk electrodes revealed an obviously different electrochemical response from that measured at the bare GC disk electrode.

For a clearer exploration of the difference in response of the different nano-Au (and/or nano-MnOx)/GC disk electrodes, Fig. 7 compares the steady-state hydrodynamic voltammograms for the ORR, measured in O₂-saturated 0.5 M KOH, at (a) bare GC, (b) nano-MnOx/GC, (c) nano-Au/GC, (d) nano-MnOx/nano-Au/GC, and (e) nano-Au/nano-MnOx/GC disk electrodes ($\phi = 3.0$ mm) at



Figure 6. Steady-state voltammograms for the ORR, measured in O₂-saturated 0.5 M KOH, at (a) bare GC disk, (b) nano-MnOx/GC disk, (c) nano-Au/GC disk, (d) nano-MnOx/nano-Au/GC disk, and (e) nano-Au/nano-MnOx/GC disk ($\phi = 3.0 \text{ mm}$)–Pt ring electrodes (RRDE) at rotation rates of (a) 200, 400, 800, 1200, 1600, and 2000 rpm; (b) 200, 400, 800, 1200, and 2400 rpm; (c) 200, 400, 800, and 1200 rpm; (d) 200, 400, 800, and 1200 rpm; and (e) 200, 400, and 800 rpm (from inner to outer). The Pt ring was potentiostated at +0.5 V vs Ag/AgCl/KCl(sat). Potential scan rate of the disk electrode was 10 mV s⁻¹. The electrodeposition conditions used for MnOx and Au nanoparticles were the same as in Fig. 1.

0

0

rotation rate of 400 rpm. The currents of the Pt ring (potentiostated at +0.5 V, corresponding to the oxidation of hydrogen peroxide produced at the individual disk electrodes) are shown at the upper side of Fig. 7 (curves marked a'-e'). The voltammograms for the ORR at the Pt disk–Pt ring electrode is also shown for comparison (curves f and f'). A comparative inspection of the RRDE voltammograms of Fig. 7 revealed some interesting points:

1. Significantly different wave forms of the disk current with a two-limiting-current region (curves c and d) and a wide-limiting-current region (curve e).

2. Different responses of the ring currents with maxima (curve c') and a rather large value throughout the entire potential window (curve a').

3. A positive shift of the onset of the ORR to a different extent at



Figure 7. RRDE voltammograms for the ORR, measured in O₂-saturated 0.5 M KOH, at (a) bare GC, (b) nano-MnOx/GC, (c) nano-Au/GC, (d) nano-MnOx/nano-Au/GC, and (e) nano-Au/nano-MnOx/GC disk electrodes ($\phi = 3.0$ mm). Curve f measured at Pt-disk electrode. Rotation rate 400 rpm. Potential scan rate of the disk electrode 10 mV s⁻¹. Curves a'-f' represent the corresponding Pt-ring currents (polarized at +0.5 V). The electrodeposition conditions used for MnOx and Au nanoparticles were the same as in Fig. 1.

the different nano-Au(and/or nano-MnOx)/GC disk electrodes. That is, the nano-Au/nano-MnOx /GC disk electrode (curve e) showed the most positive shift, and the ORR current begins to flow at potential of ca. -0.05 V vs Ag/AgCl/KCl(sat), which is a few millivolts more positive than that obtained at the bare Pt disk (curve f).

4. Entirely different current responses at the nano-Au/nano-MnOx/GC disk electrode (curve e) and its "mirror image" nano-MnOx/nano-au/GC disk electrode (curve d). A possible explanation for this observation is that in the latter case (i.e., the nano-MnOx/ nano-Au/GC electrode, curve d) the electrodeposition of MnOx is believed to occur at the bare portion of GC substrate and partly at the predeposited Au nanoparticles. This may lead to a partial deactivation of the Au nanoparticles toward the ORR, being demonstrated as the slightly negative shift of the onset potential of the ORR. However, the beneficial effect of MnOx electrodeposition in the case of nano-MnOx/nano-Au/GC electrode (i.e., curve d) over the nano-Au/GC (curve c) is the noticeable increase in the disk current due to the occurrence of the catalytic disproportionation of the electrogenerated hydrogen peroxide (HO₂) within the nanochannels of the MnOx texture. For the nano-Au/nano-MnOx/GC electrode (curve e) the electrodeposition of Au nanoparticles onto the nano-MnOx/GC electrode causes two effects compared to its mirror image (i.e., nano-MnOx/nano-Au/GC, curve d): (i) the pronounced positive shift of the ORR peak potential and (ii) the loss of the catalytic activity of the MnOx for the disproportionation of HO₂, demonstrated as a decrease in the disk current. This might originate from the blocking of the nanochannels of the MnOx texture by the subsequent electrodeposition of the Au nanoparticles. Further studies are underway to optimize the loading level of both species, i.e., MnOx and Au nanoparticles in the proposed binary catalyst.

The fact that an increase of the disk current in the case of the nano-MnOx/GC electrode compared to the bare GC disk electrode (see curves b and a, respectively) is associated with a decrease in the corresponding ring current (see curves b' and a') is attributed to the



Scheme 1. Schematic illustration of the possible reduction pathways of O₂ in alkaline media. The subscripts (a) and (b) refer to adsorbed state and bulk solution species, respectively, and the superscript (*) refers to the electrodevicinity species. The *ks* are the rate constants of the relevant steps.

catalytic decomposition of hydrogen peroxide (represented by Eq. 2) by the MnOx nanotexture electrodeposited onto the GC electrode. In this case, no electrocatalytic enhancement is observed in terms of shift of the onset potential of the ORR. Thus, the ORR is taking place mainly at the bare portion of the GC disk electrode. The nano-Au/nano-MnOx/GC disk electrode (marked e) showed the ORR at potential close (or slightly more positive) to that obtained at the Pt disk electrode (curve f). The nano-MnOx/nano-Au/GC disk electrode (marked d) showed the largest disk current for the ORR among the examined electrodes concurrently with the corresponding smallest ring current (curve d'), although the onset potential of the ORR is negative compared to that at its mirror-image disk electrode (compare with curve e). This indicates a significant contribution of the four-electron reduction pathway of O_2 (to OH⁻) at this electrode (curve d).

Thus, the sequence of the electrodeposition of both Au and MnOx nanoparticles onto the bare GC disk electrodes plays an essential role in determining the overall performance of the electrode toward the ORR. For the purpose of the quantitative assessment of the total number of electrons (*n*) exchanged at the different disk electrodes during the ORR, the general mechanism shown in Scheme 1 could be considered which represents the possible reduction pathways of O₂ (either two- or four-electron) in alkaline media.^{29,30}

The ratio of the disk and the ring currents is governed by the values of the k values

$$NI_{\rm D}/I_{\rm R} = [1 + 2k_1/k_2 + A + (k_6/Z\omega^{1/2})A]$$
[3]

where $A = (2k_1/k_2k_5)(k_{-2} + k_3 + k_4) + (2k_3 + k_4)/k_5$, *N* and ω are the collection efficiency and the rotation rate of the RRDE electrode (rad s⁻¹), respectively, and Z = 0.62, $D^{2/3} v^{-1/6} [D$ is the diffusion coefficient (cm² s⁻¹) and v is the kinematic viscosity (cm² s⁻¹)]. This equation shows the highly complicated dependency of the NI_D/I_R ratio on the *k* values. A value of unity of this ratio is expected if the one-step, two-electron reduction of O₂ (to HO₂⁻) occurs exclusively, at which $k_1 = 0$ and $k_3 + k_4$ is close to zero. This ratio tends to infinity if the one-step four-electron reduction of O₂ (to OH⁻) takes place exclusively, at which $k_2 = 0$. Accordingly, the number of electrons, *n*, exchanged during the ORR is inherently related to this ratio

$$n = 4 - 2I_{\rm R}/NI_{\rm D}$$

$$\tag{4}$$

where n = 4 if $I_R = 0$ and n = 2 if the ratio $I_R/NI_D = 1$. Figure 8 shows the variation of the ratio I_R/NI_D vs the disk electrode potential. Inspection of this figure reveals that the values of I_R/NI_D remain very close to unity for the case of the GC disk electrode (case a), indicating the exclusive two-electron reduction of O₂ to hydrogen peroxide. The lowest values of I_R/NI_D were obtained for the case of the nano-MnOx/nano-Au/GC disk electrode (case d) over a wide



Figure 8. Variation of the I_R/NI_D ratio with the disk electrode potential at (a) bare GC, (b) nano-MnOx/GC, (c) nano-Au/GC, (d) nano-MnOx/nano-Au/ GC, and (e) nano-Au/nano-MnOx/GC disk electrodes ($\phi = 3.0$ mm). Curve (f) represents the ratio measured at the Pt-Pt RRDE. The notations are the same as Fig. 7.

potential range of ca. -0.2 to -0.7 V vs Ag/AgCl/KCl(sat) among the examined electrodes. This indicates a significant contribution of the four-electron reduction pathway for the ORR at a relatively less negative potential. Beyond -0.7 V (i.e., at more negative potential) this ratio $(I_{\rm R}/NI_{\rm D})$ approaches zero, indicating the exclusive reduction of molecular oxygen to water (via HO₂ as an intermediate). A significant increase in the value of the ratio of $I_{\rm R}/NI_{\rm D}$ was obtained in the case of the nano-Au/nano-MnOx/GC disk electrode (case e). Thus, the electrodeposition of Au nanoparticles onto the nano-MnOx/GC electrode is believed to retard the catalytic disproportionation activity of the underlying MnOx nanotexture, although it causes a significant positive shift of the onset potential of the ORR. The electrodeposition of MnOx nanoparticles onto the nano-Au/GC electrode caused a significant negative shift of the onset potential of the ORR, but an increase in the catalytic disproportionation activity of the electrode was also observed. This negative shift might be reasonably assigned to the coating of the Au nanoparticles initially electrodeposited onto the GC by the subsequent electrodeposition of the MnOx nanotexture. Thus it is believed that optimum design of both catalysts onto the GC substrate would result in an electrode which compromises both advantages of the shift of the ORR to the positive direction of potential caused by Au nanoparticles and the excellent catalytic disproportionation activity caused by the MnOx nanotextures, leading ultimately to an apparent four-electron reduction pathway of O₂.

Conclusions

A binary catalyst composed of Au and manganese oxide (MnOx) nanoparticles electrodeposited onto GC substrates has been proposed for the ORR in alkaline medium. The sequence of the electrodeposition of both species was found to play a vital role in determining the reduction pathway of oxygen. While MnOx enhances the catalytic disproportionation of the electrogenerated hydrogen peroxide, Au nanoparticles were found to cause a significant positive shift of the onset potential of the current flow of the ORR. The proposed binary electrocatalyst allowed an apparent four-electron reduction of molecular oxygen at potential very close to that obtained at Pt electrocatalyst.

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