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A novel electrochemical strategy for developing alkaline air electrodes by a combined use of dual functional catalysts

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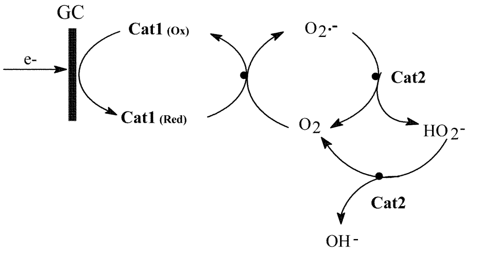
A novel electrochemical strategy for the development of new alkaline air electrodes has been proposed based on a combined use of dual catalysts for redox-mediating O_2 reduction and disproportionating the reduction intermediates, *i.e.*, superoxide and peroxide in alkaline media.

A four-electron reduction of O_2 with a low over-potential has been a long-standing goal in the development of air electrodes used for energy conversion technologies, such as metal–air batteries and fuel cells.[1] A concept based on the electrocatalysis to facilitate the electron transfer of $2e^-$ or $4e^-$ reduction of O_2 as well as to accomplish an apparent four-electron reduction of O_2 by utilizing a catalyst to disproportionate the two-electron reduction product has been anticipated to be potential for accomplishing the above purpose and has thus evoked numerous innovative catalyst designs, such as, metal macrocyclic complexes, metal alloy, and metal particles.[2] However, very few catalysts have been demonstrated to be capable of effecting the four-electron reduction of O_2.[3]

Our previous attempts to clarify the mechanism of alkaline air electrodes currently used in metal–air batteries have revealed that manganese oxides, the catalysts used in such electrodes, possess an excellent bifunctional catalytic activity toward the sequential disproportionation of reduction intermediates in O_2 reduction, *i.e.*, superoxide ($O_2^{\cdot -}$) and peroxide (HO_2^-), and such bifunctional catalytic activity, coupled with one-electron reduction process of O_2 reduction, substantially effects a quasi-four-electron reduction of O_2 at alkaline air electrodes.[4] Based on this finding, we propose here a novel and facile electrochemical strategy suitable for versatile development of new non-platinum-based alkaline air electrodes. The strategy, as schematically depicted in Scheme 1, is based on rationally combining a redox-mediated electrochemical process with a catalyzed sequential disproportional processes for the reduction intermediates to achieve a quasi-four-electron reduction of O_2 at the carbon-based alkaline air electrodes at a potential close to the thermodynamically permitted value.

We demonstrate the promising features of such strategy by utilizing a cobalt macrocyclic complex of cobalt tetra-amino-phthalocyanine (CoTAPc) for redox-mediating the O_2 reduction and MnOOH[5] as a catalyst accelerating the sequential disproportionations of reduction intermediates, *i.e.*, $O_2^{\cdot -}$ and HO_2^-.

As can be seen from Fig. 1-C, O_2 reduction occurs at −0.50 V on glassy carbon (GC) electrode (curve 1), which can be ascribed to the apparent two-electron reduction of O_2 to HO_2^- with $O_2^{\cdot -}$as the intermediate.[6] MnOOH used is electrochemically inactive (Fig. 1-A), but its excellent bifunctional catalytic activity toward the sequential disproportionation of the produced $O_2^{\cdot -}$ and HO_2^- obviously increases the peak current at −0.50 V on the GC electrode (curve 3); the re-reduction of the recycled O_2 from the sequential disproportionation reactions (Scheme 1) increases the reduction current. On the other hand, CoTAPc is electroactive with a pair of redox peaks around −0.25 V *vs*. Ag/AgCl (Fig. 1-B), which shows a good catalytic activity for redox-mediating O_2 reduction as can be evident from the positive shift of the potential for O_2 reduction at the Nafion- and CoTAPc/Nafion-modified GC electrodes (curves 1 and 2). The product of this CoTAPc-mediated reduction of O_2 was further diagnosed by using superoxide dismutase (SOD), an enzyme that catalyzes the disproportionation of $O_2^{\cdot -}$ into O_2 and HO_2^-.[7] Similar to those reported previously, we found that the additional immobilization of SOD on the CoTAPc/Nafion-modified GC electrode clearly increases the peak current at −0.25 V for O_2 reduction (not shown), indicating that such process mainly experiences one-electron reduction pathway producing $O_2^{\cdot -}$, which is somewhat stable in concentrated alkaline media employed in alkaline air electrodes.[8] The efficient catalytic activity of MnOOH toward the sequential disproportionations of the produced $O_2^{\cdot -}$ and HO_2^- (Scheme 1) results in an efficient cycle of the O_2 molecule in a whole reaction and subsequently the peak current is increased (curve 4). This, coupled with one-electron reduction of O_2 electromediated by CoTAPc, could eventually evoke a quasi-four-electron reduction process at a positively shifted potential, provided a large amount of MnOOH is used.



Scheme 1 Schematical depiction of electrocatalytic reduction of O_2 with dual catalysts in alkaline media.

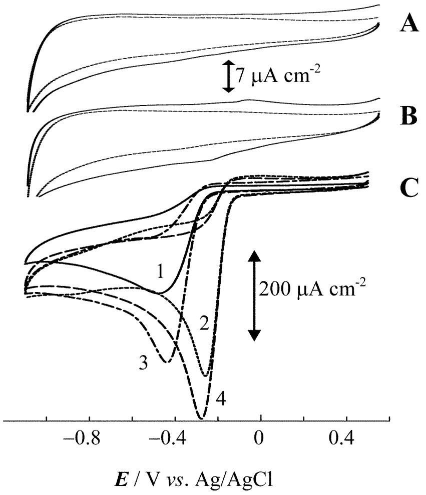


Fig. 1 Cyclic voltammograms (CVs) at Nafion- (1), CoTAPc/Nafion- (2), MnOOH/Nafion- (3) and CoTAPc/MnOOH/Nafion- (4) modified GC electrodes in O_2-saturated 0.10 M KOH solution. (A) and (B) represent CVs at Nafion-(dotted line), MnOOH/Nafion-(solid line, A) and CoTAPc/Nafion-(solid line, B) modified electrodes in N_2-saturated 0.10 M KOH solution. Scan rate: 100 mVs^{-1}. The surface coverage of MnOOH and CoTAPc are 1.50 mg cm^{-2} and 1.7 × 10^{-10} mol cm^{-2}, respectively.

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The above strategy with dual catalysts could be further demonstrated by rotating ring-disc electrode (RRDE) voltammetry as shown in Fig. 2. Similar to those obtained with CV (Fig. 1), at Nafion-modified GC electrode O_2 is reduced around -0.50 V to produce HO_2^- *via* the $O_2^{\cdot -}$ pathway, in which HO_2^- could be detected at the ring electrode (curve 1′). At the GC disc electrode modified with CoTAPc/Nafion, O_2 reduction starts at more anodic potential of *ca.* -0.30 V as expected from the redox-mediation property of CoTAPc (curve 2). However, such a mediated process could not carry a four-electron reduction of O_2 as it still produces a large current at the ring electrode (curve 2′). The combined use with MnOOH on the disc electrodes clearly increase the disc currents at the GC electrode modified either with Nafion or CoTAPc/Nafion (curves 3 and 4), while the corresponding ring currents decrease (curves 3′ and 4′) accordingly. The excellent bifunctional catalytic activity of MnOOH toward the reduction intermediates, *i.e.*, $O_2^{\cdot -}$ and HO_2^-, well explain these observed results. In addition, a comparison of RRDE obtained on our present air electrode (curve 4) with those on Pt nano-particles (curve 5), which is a typical catalyst for the four-electron reduction of O_2, clearly indicates that the present electrode based on the novel electrochemical strategy could effect almost the same four-electron reduction of O_2 as that at Pt nano-particles.

A good tolerance against methanol and glucose crossover is one of the striking features of the as-prepared air electrode as shown in Fig. 3-A. Methanol has been considered to be a promising fuel in fuel cells. In such cells with a Pt-based air electrode, a membrane is generally needed to prevent methanol from travelling to the Pt air electrode. However, some methanol molecules still pass through the membrane and are oxidized at the Pt air electrode, which causes a serious crossover and lowers the cell voltage.[9] Superior to the Pt-based air electrode, at which the oxidation of methanol fuel starts at a potential close to that of O_2 reduction as shown in Fig. 3-B, O_2 reduction is largely separated from the oxidation of methanol at the present electrode (Fig. 3-A), suggesting its simple, direct use in a cell without membranes suppressing methanol crossover. In addition, glucose, which is also a promising fuel for biofuel cells,[10] could be used in combination with the present air electrode without membranes, because it is oxidized at a potential far from that of O_2 reduction (curve 3, Fig. 3-A).

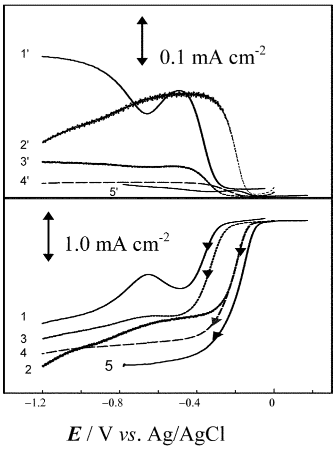

Fig. 2 RRDE voltammograms for O_2 reduction at Nafion- (1), CoTAPc/Nafion- (2), MnOOH/Nafion- (3), CoTAPc/MnOOH/Nafion- (4) coated GC disc electrodes and Pt nano-particles loaded on GC disc (5) in O_2-saturated 0.10 M KOH solution. Electrode rotation rate: 400 rpm. Potential scan rate: 10 mV s^{-1}. The Pt ring electrode was polarized at +0.50 V. Collection efficiency of the RRDE: 0.31. Pt nano-particles (23Å) are supported with carbon with a mass ratio of 46.3 (Pt) to 53.7 (carbon).

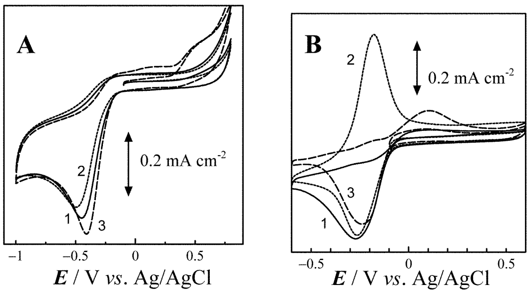

Fig. 3 CVs obtained at CoTAPc/MnOOH/Nafion-modified GC (A) and Nafion-modified Pt (B) electrodes in O_2-saturated 0.10 M KOH solution in the absence (1) and presence of (2) 20 mM methanol or (3) 10 mM glucose. Scan rate: 100 mV s^{-1}.

In summary, we have demonstrated a novel electrochemical strategy for extensively developing new alkaline air electrodes based on a combined use of dual catalysts for redox-mediating O_2 reduction and for sequentially disproportionating the reduction intermediates into O_2 and finally into OH-. The as-prepared air electrode almost provides a quasi-four-electron reduction of O_2, bearing a good comparison with the conventional platinum-based air electrodes with superiority in its high methanol and glucose tolerance. The present concept would be versatile for extensive development of new non-platinum-based air electrodes for alkaline fuel cells and metal–air batteries because the materials involved in the electro-catalytic system could be smartly screened and intentionally designed.

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