Oxygen Reduction Characteristics on Pyrolytic Graphite Electrodes Modified with Electro-polymerized Salen Compounds

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Electro-polymerized cobalt salen compounds on pyrolytic graphite electrodes were first tested as oxygen reduction catalysts in aqueous solutions of various pH. From electrochemical measurements it was revealed that although in acidic media the catalyst performance deteriorated, the performance in neutral and basic media was relatively good as compared to that of platinum, the best catalyst for this reaction.

Oxygen reduction is of basic and practical importance in such fields as fuel cell cathodes, synthetic processes as well as biological systems like respiratory cycles in living organs, and has attracted much research interest. However, research efforts to get knowledge about the detailed mechanism and to attain higher efficiencies by use of artificial catalysts are still left for major improvements. This is because oxygen reduction process involves multi-electron transfer steps, and therefore, a high activation barrier for its occurrence. The most efficient catalyst is platinum, but owing to its high cost the reduction of catalyst loading and search for alternatives are of contemporary interest. In this context several metal-centered organic ligands are studied such as porphyrin compounds, phthalocyanines and Schiff base compounds.[1-4]

We have been developing cobalt porphyrin ion pair complexes for potential use in oxygen sensors or fuel cell cathodes.[5,6] To achieve a good catalytic performance fulfilling also practical economic requirements, simple structure of the metal complex is essential for synthetic reasons. In this sense CoN_4 unit in the chelate structure apparently was of vital importance, and this unit was found to have played a significant role in catalytic activity for oxygen (O_2) reduction.[6-8] To know about the correlation between ligand structure and the catalytic activity for O_2 reduction, we also investigate other types of ligands, and one of potential candidates is metal-N_2O_2 chelate compounds. In this paper we report electro-polymerized cobalt salen compounds on basal plane of high density pyrolytic graphite (BHPG) electrodes and its O_2 reduction activity in aqueous solutions.

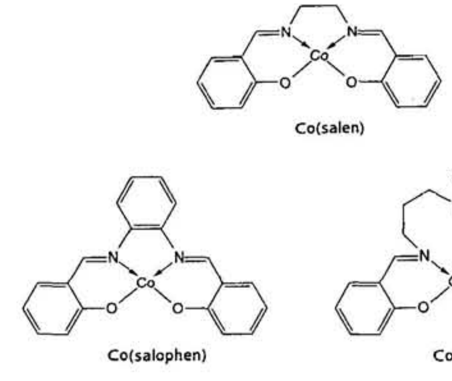

Figure 1. Structures of cobalt salen compounds.

N,N'-Bis(salicylidene)ethylenediaminocobalt(II) [denoted as Co(salen)] and its analogues were used as purchased (Aldrich). Structures of compounds are shown in Figure 1 together with their abbreviations. Tetramethyl-ammonium tetrafluoroborate ($TMABF_4$, Aldrich) was dehydrated at 65 ℃ in a vacuum. Electro-polymerization of Co(salen) compounds was performed on BHPG from anhydrous acetonitrile (AN, Kanto Chemicals) with 2 mM cobalt salen compounds and 50 mM $TMABF_4$ at 25 ℃. Electrochemical cell was composed of the BHPG working electrode (apparent area 0.20 cm^2), the Pt counter electrode and the Ag "pseudo"-reference electrode, and the potential was scanned 5 times between −1.7 and 1.7 V at a scan rate of 0.1 Vs^{-1}, the electrolyte being deaerated by Ar bubbling.

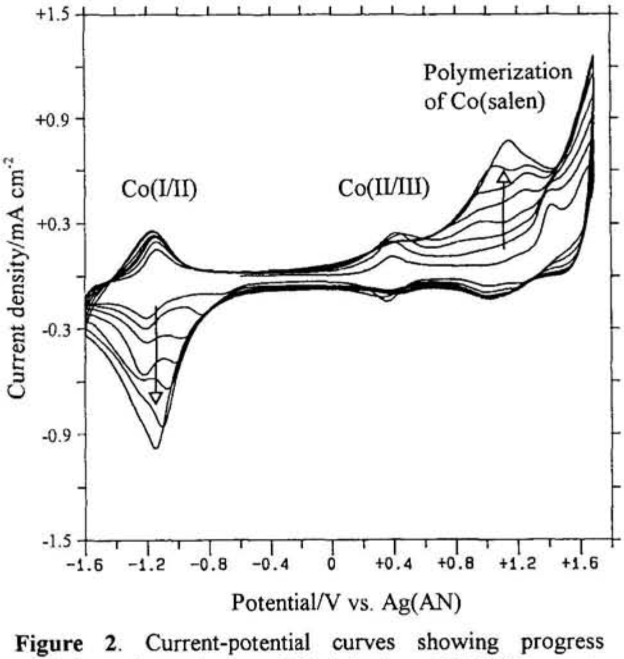

Figure 2. Current-potential curves showing progress of oxidative polymerization of Co(salen) on BHPG (apparent area 0.20cm^{-2}). Solution: Ar saturated AN solution with 2mM Co(salen) and 50mM $TMABF_4$. Scan rate: 0.1 Vs^{-1}.

Figure 2 represents current-potential curves for Co(salen) polymerization by cyclic scanning. At around 1.35 V, the current peaks for Co(salen) polymerization develop, while Co(II/III) and Co(I/II) peaks appeared at around 0.4 V and -1.2 V, respectively, the former diminished while the latter increased by repeated scans. A greenish film was observed on BHPG.

Film formation of poly[Co(salen)] was confirmed by observation of Co(I/II) peaks in a Co(salen) free electrolyte. The amount of poly[Co(salen)] deposited by 5 scans was calculated to be 5×10^{-8} mol cm^{-2} from the charge of the Co(I/II) peak. XPS spectra showed that Co 2p and N 1s peaks became narrow with polymerization.

Cyclic voltammograms (CVs) for O_2 reduction on BHPG electrodes modified with poly[Co(salen)] or analogues were measured in aqueous solutions of various pH values saturated with 1 atm O_2. A current due to O_2 reduction increased around 0.6-0.9 V vs. RHE (hydrogen electrode in the same solution) depending on pH, showing good catalytic performance. The highest current and the most positive potential for O_2 reduction were attained in basic media. Among the catalysts tested, poly[Co(salen)] was most active for O_2 reduction. CV showed good reproducibility except in acidic solutions where catalytic activity degraded in a single scan.

The potential-current relations as measured by rotating ring-disk electrode (RRDE) differed between acidic media and neutral or basic media. In acidic media, O_2 reduction current occurred with one plateau, but in basic media it occurred with two plateaus. In the first plateau, H_2O_2 formation prevailed while in the second plateau H_2O formation predominated (Figure 3).

The efficiency of O_2 to H_2O conversion, *%H₂O*, was measured using RRDE at a scan rate of 0.01 Vs^{-1}. Half-plateau potential for O_2 reduction and the kinetic current j_k at this potential were obtained from Koutecky-Levich plots. Table 1 summarizes the kinetic parameters as compared with those measured on smooth Pt. In acidic and neutral media, the performance of poly[Co(salen)] and analogues were all much inferior to Pt. Especially in acidic media, the catalytic activity degraded quickly when poly[Co(salen)] or analogues were once polarized in cathodic direction. In basic media, on the other hand, organic catalysts showed significant improvements in performances as compared with acidic and neutral media. Especially the half-plateau potential was close to that of Pt. To our knowledge, it was not reported before that electro-polymerized salen compounds exhibited catalytic activities for O_2 reduction in aqueous solutions. The results here show that metal salen compounds can be feasible catalysts for O_2 reduction, with simple structure and low-cost features. It should also be noted that a new preparation method of modified electrodes by electro-polymerization of salen compounds can be applicable to such systems as fuel cell cathodes or oxygen sensors. Further research is in progress to investigate the detailed mechanism of O_2 reduction and the cause of degradation of the catalysts in acidic media, and to improve further the catalytic performances.

Table 1. Results of RRDE measurements for O_2 reduction at poly[Co(salen)] and analogues modified BHPG electrodes in several kinds of solutions

Solution	Catalyst	$\%H_2O$ [a]	$E_{p,1/2}$ [b] /V vs.RHE	j_k [b] /mAcm^{-2}
0.05M H_2SO_4 (pH=1.2)	poly[Co(salen)]	21	0.48	0.27
	poly[Co(salophen)]		0.28	0.26
	poly[Co(salpr)]	32	0.30	0.34
	Pt [c]	94	0.74	8.3
0.1M KH_2PO_4/K_2HPO_4 (pH=7.0)	poly[Co(salen)]	39	0.46	1.0
	poly[Co(salophen)]	33	0.39	2.7
	poly[Co(salpr)]	30	0.29	2.6
	Pt [c]	98	0.72	5.6
0.1M NaOH (pH=14.1)	poly[Co(salen)]	67	0.75	1.2
	poly[Co(salophen)]	60	0.77	1.6
	poly[Co(salpr)]	67	0.70	0.7
	Pt [c]	96	0.80	14

[a] At plateau potentials, 100 rpm. [b] At half-plateau potentials.
[c] Smooth platinum disk.

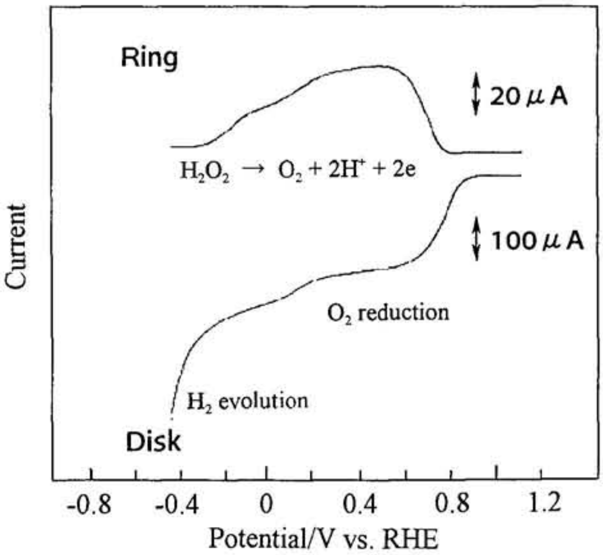

Figure 3. Ring and disk currents at a Pt ring (area 0.283 cm^2)/poly[Co(salen)] modified BHPG disk (area 0.0314 cm^2) electrode in 0.1 M NaOH saturated with 1 atm O_2. Collection factor N = 0.38. Ring potential: 2.05 V, scan rate of disk potential: 0.01 Vs^{-1}, rotation speed: 100 rpm.

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