

## Oxygen Reduction at the Rare-earth Phthalocyanine-modified Glassy Carbon Electrode in Aqueous Media

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### Introduction

The oxygen reduction reaction (ORR) is the cathode reaction of fuel cells such as the proton exchange membrane fuel cell (PEMFC). Due to the problems associated with costs and platinum resources, it is highly desired to utilize non-noble metals as the electrode catalysts; organometallic macrocycles such as porphyrins and phthalocyanines have been considered as an alternative to platinum-based catalysts, because they are highly stable and have reversible redox properties suitable for the electrocatalyst for the ORR [1]. In addition, these macrocyclic catalysts are expected to be methanol-insensitive during oxygen electroreduction in a direct methanol fuel cell (DMFC). In this respect, transition metal phthalocyanines have been thoroughly examined for their activity toward the ORR. However, there are scarce reports on the catalytic activity of the rare-earth phthalocyanines toward the ORR. We have continued investigation on the electrochemical and optical properties of rare-earth phthalocyanines. The present work explores the catalytic activities of the title complex for the ORR in aqueous electrolyte solutions.

### Experimental

Bis(phthalocyaninato)lanthanide (III) complexes,  $[\text{LnPc}_2]^{z-}$  ( $\text{Ln}=\text{Nd}, \text{Yb}$  or  $\text{Gd}$  and  $z=-1$ ) were synthesized as tetrabutylammonium (TBA) salts according to the procedure described in ref.2. We fabricated  $\text{LnPc}_2$ -modified GC electrodes by the following two methods: An aliquot of acetone solution of the  $\text{TBA}[\text{LnPc}_2]$  (1 mM) was cast on the GC disk electrode surface with a microsyringe and the solvent was dried (cast-coated GC). Another electrode is the dip-coated GC, which was prepared by soaking bare GC electrode in the solution of 1 mM  $\text{TBA}[\text{LnPc}_2]$  dissolved in acetone for 30 min in order to establish adsorption equilibrium. After washed the electrode with pure acetone, the solvent was dried and used.  $\text{Ag} | \text{AgCl} | \text{KCl} (\text{sat})$  was used as the reference electrode and all the potentials were quoted against this electrode.

### Results and discussion

The solid curve in Fig. 1 shows the cyclic voltammogram (CV) of the  $\text{NdPc}_2$  modified GC electrode (dip-coated GC) measured in  $\text{O}_2$  saturated 0.5 M  $\text{H}_2\text{SO}_4$  solution. Compared with the response obtained at the bare electrode (dotted curve), it is obvious that the  $\text{O}_2$  reduction starts at more positive potentials than the bare electrode. Since the potential coincides with the redox potential of the complex, we can consider that the complex catalyzes the electrochemical  $\text{O}_2$  reduction. According to the rotating ring-disk electrode (RRDE) experiments, the main product was found as the hydrogen peroxide, but four-electron reduction of  $\text{O}_2$  was also suggested to take place as well as the two-electron reduction process depending on the potential. The stability of the electrode in strong acid solutions was,

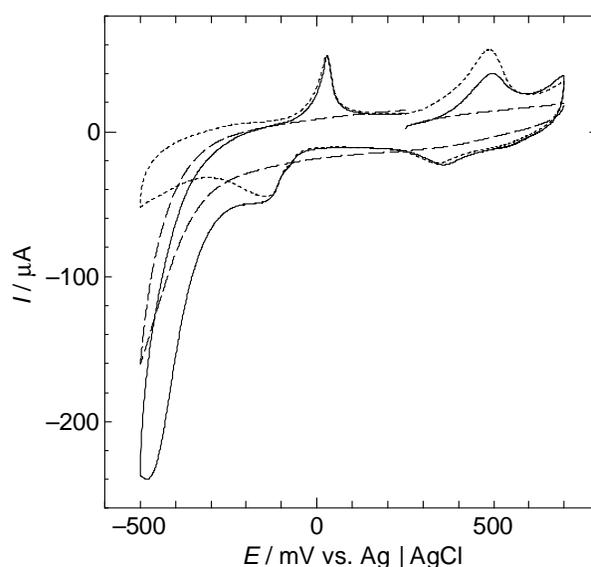
unfortunately, not good and degraded during several tens of potential sweeps. On the other hand, fairly good stability was attained in neutral solutions. In alkaline solutions, the electrode was quite stable, but the catalytic activity toward  $\text{O}_2$  reduction greatly depressed since the complex becomes electro-inactive in such high pH solutions. We also tried similar experiments using cast-coated GC electrodes. Although the amount of the complex deposited on the electrode surface was larger, the catalytic current was found to be smaller than those observed at the dip-coated electrode. This might be ascribed to the compactness of the deposits, suggesting the importance of controlling the surface geometry of the complex to attain most efficient catalytic activity. Dependence on the central rare-earth metal ions will also be discussed.

### References

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**Fig. 1** Cyclic voltammograms obtained at cast-coated GC electrode in the  $\text{O}_2$  saturated (solid curve) and  $\text{N}_2$  saturated (dotted curve) 0.5 M  $\text{H}_2\text{SO}_4$  solutions. Dashed curve was obtained at bare GC electrode in the  $\text{O}_2$  saturated solution. Sweep rate was  $100 \text{ mV s}^{-1}$ .