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Nanostructured Manganese Oxide Catalysts Prepared by Pulsed Laser Ablation

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Introduction

Recently, transition-metal oxides have attracted considerable interest because of their unique properties. In catalysis field, they have received attention as electrocatalyst for metal/air batteries and fuel cells, and it is reported that catalytic activity of transition-metal oxides depends on nanostructures and chemical compositions [1]. However, it is difficult to control both nanostructures and chemical compositions of transition-metal oxides using thermal equilibrium chemical process. On the other hand, pulsed laser ablation (PLA) in background gases has advantages in the deposition of functional oxides, because interactions between ablated species and the background gases result in not only physical collisions but also chemical reaction control [2].

From this viewpoint, we apply the PLA process to the deposition of nanostructured manganese oxides (MnOx). We characterized the catalytic properties of MnOx to verify the potential for nano-catalyst.

Experimental

Nanostructured MnOx was deposited using the PLA process (Fig. 1). An argon-fluoride (ArF) excimer laser beam (wavelength: 193nm, pulse energy: 50 mJ) was focused onto a sintered MnO target. During the laser ablation, background gas (He or He/O_2 mixtures) was introduced into the chamber and was maintained at a constant pressure (0.5 - 5.0 Torr). Then, ablated species were condensed in the gas phase, and were deposited on substrates.

The structures of the deposits were observed using scanning electron microscope (SEM) and transmission electron microscope (TEM). The chemical compositions of the deposits were estimated using x-ray absorption fine structure (XAFS) measurement.

We measured the catalytic activities of the nanostructured MnOx on oxygen reduction in alkaline solutions. For cyclic voltammetry, a computer-controlled electrochemical system (ALS 750*i*, ALS/CH Instruments) was used. A platinum wire was employed as the auxiliary electrode, and the reference electrode was Ag/AgCl (KCl saturated). A standard three-compartment glass cell was used for electrochemical measurements.

Results and discussion

Structural characterization of deposits was carried out using SEM. We observed the structural transition from thin films to agglomerates with larger surface area by varying the background gas pressures. Moreover by varying the mixture ratio of oxygen, the agglomerates have different nanostructures [3]. These results were attributed to physical and chemical reactions in plasma plume of the laser ablation. Furthermore, we analyzed the detail of the agglomerates using TEM. Crystallinity of nanoparticles forming the agglomerates were evidently single crystalline because we found clear lattice plane [4].

Figure 2 shows cyclic voltammograms of the nanostructured MnOx modified glassy carbon (GC) electrode on oxygen reduction in 0.1 M KOH aqueous solutions. This nanostructured MnOx was deposited in pure He gas, showed columnar structure. The reduction peak current per weight, of nanostructured MnOx modified electrode was about ten times larger than that of MnO powder modified electrode. Furthermore, over potential of nanostructured MnOx modified electrode on oxygen reduction was reduced by 0.04 V.

This significant catalytic activity might be due to the specific nanostructures, and suggests the potential for highly active nano-catalyst.

References

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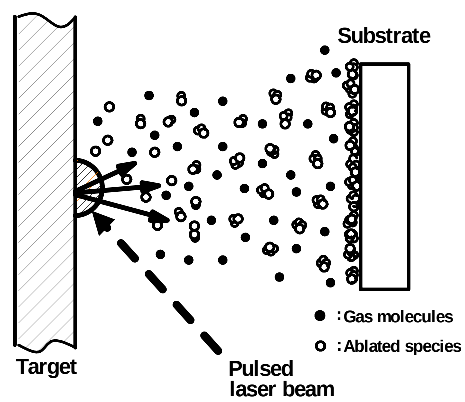

Fig. 1 Shematic view of PLA process.

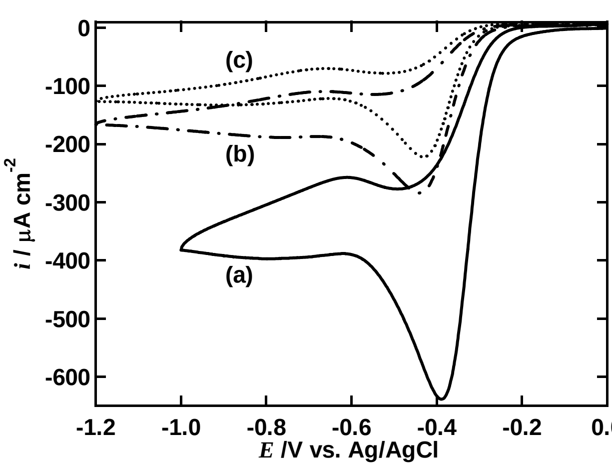

Fig. 2 Cyclic voltammograms obtained at (a) nanostructured MnOx/ Nafion -, (b) MnO powder/ Nafion -, and (c) Nafion - modified GC electrodes, in O_2 - saturated 0.1 M KOH solution.