

Evaluation of the activity of different MnO₂ regarding oxygen reduction for metal/air battery applications

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Introduction

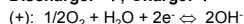
Manganese dioxide is a very important electrode material for batteries (both primary and secondary), capacitors and fuel cells operating in alkaline conditions. The role of MnO₂ in batteries and fuel cells is due its intrinsic reduction/oxidation reactions in solid state and to the catalytic effect for the oxygen reduction reaction (ORR). The electrochemical behaviour is complicated by the existence of a large variety of loosely defined MnO₂-type compounds (e.g. amorphous, α, β, γ, δ or ε - crystalline structures) and the various degrees of proton intercalation. Hence, a better way to describe γ - MnO₂ is the Ruetzchi formula: Mn(IV)_{1-a-b}Mn(III)_b□_aO_{2.4a+b}(OH)_{4a+b} where □ - denotes cation vacancy, and 0 ≤ a, b < 1.

The structural properties and the morphological features (e.g. particle size or layered thin-film) are influenced by the preparation method (thermochemical or electrochemical) and the employed conditions of temperature, pH and chemical composition of the media. In the present work the goal is to develop highly effective and rechargeable MnO₂ catalyzed positive electrodes for Zn-air batteries for use in micro-electronic applications.

Electrode reactions

The electrode reactions in a secondary Zn/air battery in concentrated alkaline solution (pH ≥ 14) are:

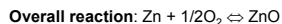
Discharge: →; **Charge:** ←



$$E^\circ = 0.4 \text{ V}_{\text{SHE}}$$



$$E^\circ = -1.25 \text{ V}_{\text{SHE}}$$



$$E^\circ_{\text{cell}} = 1.65 \text{ V at } 298 \text{ K}$$

Objectives

In spite of extensive literature, there is, in our assessment, a surprising lack of thorough electrochemical characterization of various sources of MnO₂ with evaluation of the corresponding activity toward oxygen electroreduction in gas diffusion electrodes. Therefore, the objectives of this work were as follows:

1. Cyclic voltammetry evaluation in N₂ saturated 6M KOH of four commercial MnO₂ samples (Merck, Riedel de Haen, Sigma-Aldrich and Tronox) supported on carbon Vulcan XC-72 and impregnated on either teflonated or un-teflonated Toray® carbon paper substrates.
2. Cyclic and linear voltammetry studies in O₂ saturated 6M KOH of MnO₂ gas diffusion electrodes using static and rotating-disk electrode techniques for assessment of the oxygen electroreduction activity and estimation of electrode kinetic parameters (exchange current density and Tafel slope).
3. Correlation of the observed electrochemical behaviour with structural features of the various MnO₂ electrodes revealed by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Experimental

Gas diffusion electrode (GDE):

- Substrate: Toray® carbon paper (TGP H-060): teflonated (30% PTFE) or un-teflonated
- Catalyst layer: 0.5 mg cm⁻² MnO₂ supported on 0.5 mg cm⁻² carbon Vulcan XC-72 with 20% PTFE (polytetrafluoroethylene).
- MnO₂ sources: i) Merck, ii) Riedel de Haen, iii) Sigma-Aldrich and iv) Tronox. Particle size: ~ 10 μm.
- Geometric area: 1.45 cm² disk
- Total GDE thickness: ~ 100 μm.

Electrolyte: 6M KOH: saturated with either a) N₂ or b) O₂ at atmospheric pressure.

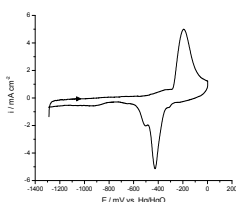
Temperature: 295 K

Potentiostat and rotating-disk electrode setup:

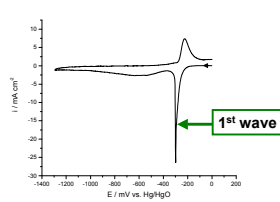
- Jaissle PG100 Bi-potentiostat
- Glassy carbon disk with GDE attached to it using electronically conductive Ag-filled epoxy glue. **Note:** Ag-filled epoxy glue was tested in 6M KOH and it was found electrochemically inactive at potentials lower than +100 mV vs. Hg/HgO, 1M KOH.
- Reference electrode: Hg/HgO, 1M KOH (MOE)
- Counter electrode: two Pt foils
- Working electrode (GDE) potential range: -1300 mV_{MOE} ≤ E < +100 mV_{MOE}
- Scan rate: between 1 mV s⁻¹ to 100 mV s⁻¹
- Rotation rate: between 0 to 4000 RPM.

Cyclic voltammetry of MnO₂ GDE with Teflonated Toray®

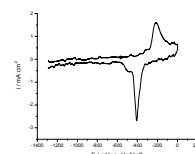
a) Merck - GDE / N₂



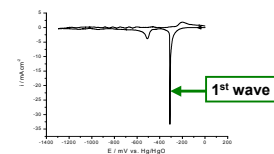
b) Merck - GDE / O₂



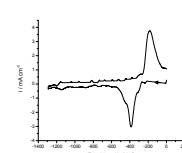
c) Riedel de Haen MnO₂ GDE / N₂



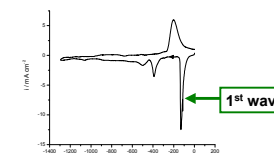
d) Riedel de Haen MnO₂ GDE / O₂



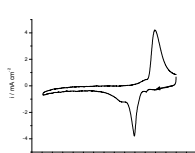
e) Sigma-Aldrich MnO₂ GDE / N₂



f) Sigma-Aldrich MnO₂ GDE / O₂



g) Tronox MnO₂ GDE / N₂



h) Tronox MnO₂ GDE / O₂

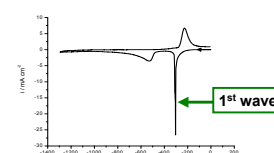
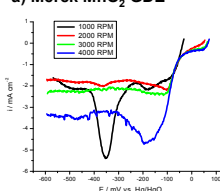


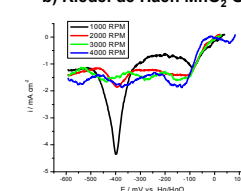
Figure 1 Cyclic voltammograms of MnO₂ GDE with teflonated Toray® carbon substrate in 6M KOH. a), c), e), g) N₂ saturated, b), d), f), h) O₂ saturated, 1st cycle. 2 mV s⁻¹.

ORR measurement on RDE: MnO₂ GDE with Teflonated Toray®

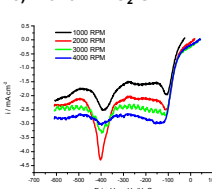
a) Merck MnO₂ GDE



b) Riedel de Haen MnO₂ GDE



c) Tronox MnO₂ GDE



d) Sigma-Aldrich MnO₂ GDE

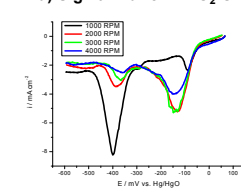


Figure 2 Effect of rotation rate on the ORR catalyzed by various MnO₂ GDEs with teflonated Toray®. 6 M KOH. O₂ saturated. 5 mV s⁻¹.

Conclusions

1. The 1st wave for O₂ reduction appears as a sharp, adsorption-type, peak in cyclic voltammetry at potentials positive vs. MnO₂ reduction peak potential of -400 mV_{MOE}.
2. The 2nd wave for O₂ reduction takes place at potentials somewhat negative vs. MnO₂ reduction peak potential of -400 mV_{SSCE}.
3. The following reaction sequence is proposed for ORR on MnO₂ GDE:
 1st step: O_{2,ad} + 2e⁻ + H₂O → HO₂⁻ + HO⁻ catalyzed by Mn(IV) [i.e. MnO₂]
 2nd step: HO₂⁻ + 2e⁻ + H₂O → 3OH⁻ catalyzed by Mn(III) [i.e. MnOOH]
4. RDE experiments support the two-step reduction. The 2nd wave in ORR, at RPM > 1000 (typically) decreases with increase of the rotation rate indicating the ejection of HO₂⁻ from the reaction layer.
5. There were difference based on MnO₂ source: The ORR 1st wave peak potentials were:
 -150 mV: Sigma-Aldrich > -300 mV: Tronox, Merck > -310 mV: Riedel de Haen.

Acknowledgement

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