The Role of Heat Treatment in Enhanced Activity of Manganese Oxides for the Electrochemical Oxygen Reduction and Evolution

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Manganese oxides and oxyhydroxides (MnOx) can exist in over 15 types of phases with Mn taking on 2+, 3+, and 4+, and mixed valent oxidation states as well as various structural configurations. (1) Recently, an increasing number of phases has been linked to high activity for the oxygen reduction reaction (ORR) (2-6) and the oxygen evolution reaction (OER) (7-12) raising the importance of MnOx catalysts to energy storage and conversion devices such as alkaline fuel cells, metal-air batteries, electrolysis cells, and photovoltaic/oxygen evolution production. To accelerate development of MnOx catalysts for these important technologies, it is necessary to determine the properties of active MnOx surfaces under reaction conditions. From thermodynamic considerations, the relevant ORR and OER bulk phases in alkaline conditions can be predicted as MnOx/MnOOH and MnOx (13) while the relevant ORR and OER surfaces have been recently proposed to be MnOx covered with ½ monolayer of adsorbed OH and MnOx covered with adsorbed O2 using density functional theory calculations. (14) These thermodynamically stable phases may or may not form in real catalysts because kinetic barriers may favour a different phase. Experimental characterization of MnOx active surfaces in real catalysts under or after exposure to reaction conditions has so far been limited to a handful of studies. Under the ORR conditions, MnOx has been shown to exist as MnOx (15) MnOx (16) and a mixture of MnIII oxide and MnO2. (12, 17) Although from thermodynamic considerations the application of OER potentials is expected to produce MnO2, exposure to more oxidative potentials relevant to the OER is most commonly associated with formation of a mixed oxide phase similar to birnessite-MnOx, which has a Mn oxidation state of ~3-3.8 (9, 11, 15) Additionally, investigations that looked at the oxidation state of Mn as a function of applied potential in the region between the ORR and the OER found that the catalysts showed either a significant change in Mn oxidation state (2, 15) or a minor change that was not detected by the employed spectroscopic technique. (16) These seemingly conflicting reports indicate that the observed phase at the ORR and the OER potentials may differ from the expected thermodynamically stable phase calculated in a Pourbaix (13) or a surface Pourbaix diagram of MnOx (14) and suggest that MnOx surface at the ORR and the OER potentials may depend on the starting phase or preparation route.

In our previous study, we demonstrated that electrodeposition of MnOx on glassy carbon followed by a heat treatment at 480°C leads formation of alpha-MnO2 phase with bifunctional activity for the ORR and the OER. Subsequent characterization of the ORR and the OER relevant surfaces using ex-situ XPS failed to reveal any differences in the Mn 2p3/2 satellite structure or the O 1s spectra of the samples relevant to the two reaction conditions, suggesting that heat treatment at 480°C limited the ability of MnOx to change oxidation state to the very top surface layer, likely on the order of one monolayer. (16) The study discussed herein will focus on understanding the effect of heat treatment temperature on the pseudocapacitive behaviour of MnOx catalysts and their activity for the ORR and the OER. In the study, we synthesize different types of MnOx surfaces by electrodepositing MnOx on glassy carbon (GC) and exposing the electrodes to five different heat treatment conditions: no heat treatment (“no ht”), heat treatment at 250°C, 350°C, 450°C, and 500°C. We then hold each of the five samples at an ORR relevant potential of 0.7 V or an OER relevant potential of 1.65 V and track the resulting oxidation state of Mn using surface sensitive ex-situ Mn L-edge XAS, a more sensitive probe for distinguishing Mn oxidation state than XPS (18) By interfacing the XAS spectra with electrochemical characterization we determine how the surface properties influence the activities for the ORR and the OER.

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