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 (MnO_x) can exist in over 15 types of phases with Mn taking on 2^+, 3^+, 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 MnO_x catalysts to energy storage and conversion devices such as alkaline fuel cells, metal-air batteries, electrolysis cells, and photoelectrochemical hydrogen production. To accelerate development of MnO_x catalysts for these important technologies, it is necessary to determine the properties of active MnO_x surfaces under reaction conditions.

From thermodynamic considerations, the relevant ORR and OER bulk phases in alkaline conditions can be predicted as Mn_2O_3/MnOOH and MnO_2,[13] while the relevant ORR and OER surfaces have been recently proposed to be Mn_2O_3 covered with ½ monolayer of adsorbed OH and MnO_2 covered with adsorbed O, 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 MnO_x 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, MnO_x has been shown to exist as Mn_3O_4,[15] Mn_2O_3,[16] and a mixture of Mn(III) oxide and MnO_2.[2, 17] Although from thermodynamic considerations the application of OER potentials is expected to produce MnO_2, exposure to more oxidative potentials relevant to the OER is most commonly associated with formation of a mixed oxide phase similar to birnessite-MnO_2, which has a Mn oxidation state of ~3.7-3.8.[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 MnO_x[14] and suggest that MnO_x 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 MnO_x on glassy carbon followed by a heat treatment at 480°C leads formation of alpha-Mn_2O_3 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 $2p_{1/2}$ 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 MnO_x 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 MnO_x catalysts and their activity for the ORR and the OER. In the study, we synthesize different types of MnO_x surfaces by electrodepositing MnO_x 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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