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Chapter 7

Manganese-Oxide Solids as Water-Oxidation Electrocatalysts: The Effect of Intercalating Cations

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A set of birnessite-type manganese oxides with both monovalent alkaline cations (Li^+ , Na^+ , K^+ , Rb^+ or Cs^+) and divalent alkaline- earth cations (Ca^{2+} or Mg^{2+}) has been synthesized using electrolytic deposition methods. X-ray diffraction gives typical birnessite-type patterns, with diffraction peaks at $2\theta = \sim 12.01^\circ$ and 24.7° assigned to (001) and (002) planes. Electron paramagnetic resonance spectra suggest differences in the stability of Mn(III) species in manganese-oxide layer, which is more stable in birnessite samples with divalent cations than samples with monovalent cations. The activity of samples for an anodic O_2 -evolution reaction is considerably affected by electrostatic potential and Lewis acidity of the monovalent cation, following the sequence of $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. While for samples with intercalating divalent alkaline-earth cations, there was slightly lower activity for O_2 evolution, which may be correlated to different stability of Mn(III) species in the birnessite layers. In addition, we observed much higher O_2 -evolution activity at an overpotential of ca. 220 – 230 mV if the samples were heat-treated between 300 – 500 $^\circ\text{C}$ once they were electrolytically deposited as LiMnO_x films. Clearly dry heating causes changes in both the crystalline structure and electronic structure of manganese-oxide layers, as indicated by associated changes in water-oxidation activity.

1. Introduction

Sunlight is a carbon-neutral energy source that daily provides $\sim 10^4$ times the current energy needs of the human population (1). Nature traps light energy as chemical energy via photosynthesis—a process of rearranging chemical bonds of water molecule to form O_2 and NADPH (a reduced form of nicotinamide adenine dinucleotide phosphate, a means of storing H_2 reducing equivalents) (2, 3). The key four-electron step occurs in the Oxygen-Evolving-Complex (OEC) in Photosystem-II (PSII), a transmembrane cofactor-protein complex embedded in the thylakoid membrane of plants and cyanobacteria (4–7). Human efforts to mimic this reaction have so far fallen short, in part because the synthetic catalysts often suffer oxidative damage during water oxidation, much as the protein in PSII becomes photodamaged.

Parallel efforts are now focusing on simple inorganic materials that regenerate themselves during the water electrolysis. Several researchers have attempted to utilize solar energy to generate electron-hole pairs in a semi-conductor that then power a catalyst. In a typical strategy, electrons are transferred to catalysts doped onto a cathode to form H_2 , which is collected and stored, and the holes are transferred to catalysts on an anode to produce O_2 , which is usually released. This electrolysis process is referred to as “water-splitting” in subsequent discussion (8–13), which focuses on the energetically expensive, four-electron oxidation step of making O_2 from H_2O .

One of the biggest challenges for an artificial solar fuel is to develop an efficient catalyst for water oxidation from metals that are abundant in the Earth. To date, the most efficient catalysts for O_2 evolving are IrO_2 and RuO_2 exhibiting high turnover frequencies (TOF), which have been investigated extensively (14–25). However, the high cost of mining these materials could limit the wide use of these noble metals as catalysts in making solar fuels. Therefore, it is essential and necessary to develop affordable and comparable efficient catalysts for O_2 evolution reaction from Earth-abundant materials like iron or manganese.

Manganese (Mn), the 10th most abundant element on the earth crust, is a key element in environment and global redox cycling processes, which enable it to serve as a plentiful cheap and clean natural resource (26). Actually, manganese has been selected by Nature as the catalyst for O_2 evolution, the OEC, which is a μ -oxo-bridged tetrameric manganese cluster Mn_4CaO_5 found in nearly all photosynthetic organisms (27–30). The OEC catalyzes water oxidation with low overpotential (η : ~ 160 mV) in near-neutral pH environment (pH 6.5) (31–33). Inspired by the OEC, many manganese complexes and particles have been synthesized and investigated as catalysts for water oxidation (34–60). In general, there are two approaches used to assess the redox suitability of these catalysts. One is an electrochemical procedure whereby catalysts are doped onto the anode electrode to measure the overpotential (η) needed for O_2 evolution (the lower η , the more valuable the catalyst becomes because the cost of generating oxygen decreases) (34–40). The second approach does not use a solid electrode. Instead, O_2 production from water is coupled to solute chemical oxidants, such as $(NH_4)_2Ce(NO_3)_6$ or $Na_2S_2O_8$, which serve as electron acceptors for homogeneous catalysts in solution or with a suspension of solid catalyst particles (48–60). Shown in Table 1 is a summary of

Najafpour et al.'s work focusing on the second reaction geometry and employing varying types of manganese-oxide nanoparticles as catalysts for water oxidation reaction (50–58, 61).

Birnessite-type manganese-oxide minerals have a layered structure consisting of edge-sharing octahedral MnO_6 , with water molecules and various cations occupying the interlayer spaces (26, 62). This open structure provides a high contact surface for the various reactive species if it serves as a catalyst (63–66). and has a well-known ion-exchange capacity (67). Varying the intercalating cation with different radii and positive charges could result in different interlayer distance (d_{001}) values and different concentrations of Mn(III) in manganese-oxide layer. These are thought to affect the activity for O_2 evolution from water oxidation reaction.

In the present work, a set of birnessite-type manganese oxide solids with both monovalent alkaline and divalent alkaline-earth cations (MMnO_x , $\text{M} = \text{Li}^+$, Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} or Ca^{2+}) are synthesized via electrolytic-deposition method. The structure and electronic properties are characterized by X-ray diffraction (XRD) and electron paramagnetic resonance (EPR) spectroscopy. The activity of these samples for the anodic water-oxidation reaction was then established via linear-sweep voltammetry (LSV) in neutral Tris-buffered solution with $\text{pH} = 7.8$. Our goal is to establish a set of correlations between structure and the overpotential η needed for O_2 evolution.

2. Experimental Procedures

2.1. Electrodeposition of Manganese Oxide Film

Birnessite-type manganese oxide was prepared via electrodeposition on fluorine-doped tin-oxide-coated glass (FTO; Hartford Glass Co. Inc., Hartford City, IN, USA), which has been described in the literature (36). Before electrodeposition, the FTO electrode (1×2 cm) was ultrasonically washed with soapy water, acetone, isopropanol alcohol and purified water (18 M Ω resistance). Electrodeposition was achieved using a Princeton Applied Research (Oak Ridge, TN, USA) Model 263 A potentiostat/galvanostat and PowerStep package software in a three-electrode system, in which Ag/AgCl (in saturated NaCl solution, 0.194 V vs NHE) was the reference electrode, FTO was employed as the working electrode with exactly 1 cm² immersing in electrolyte and nickel foam was used as the counter electrode.

Manganese-oxide solids with intercalating cations of Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} or Ca^{2+} were prepared by potentiostatic electrodeposition (on the submerged half FTO plates with area = 1×1 cm) at an initial potential of 0.8 V for 300 s (in order to improve the oxide-FTO interface by forming an interfacial film ca. < 2 nm (36)) and then holding the potential at 1.0 V vs Ag/AgCl (in saturated NaCl solution) in a bath containing electrolyte of 2 mM MnSO_4 and 0.05 M LiCl , NaCl , KCl , RbCl , CsCl , MgCl_2 or CaCl_2 , correspondingly, to obtain a stable current 0.8 mA/cm². The thickness of the film was assessed by the total deposited charge (ca. 144 mC/cm²) on the FTO plate, corresponding to ~161 nm thickness of deposited film (36). The final created brown film of manganese oxide was stored in the

corresponding electrolyte for later catalytic testing. We denote these samples as MMnO_x ($\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Mg}^{2+}$ or Ca^{2+}). To make heat-treated LiMnO_x samples, the FTO electrode (area = 1×2 cm) that had been electrolytically coated with LiMnO_x film (area = 1×1 cm) was placed on the surface of a hot plate for 2 hours exposed in air, with the temperature set as 200, 300 or 500 °C.

2.2. XRD Characterization

Powder X-ray diffraction (XRD) patterns of manganese-oxide samples (LiMnO_x , NaMnO_x and CaMnO_x) were recorded on a Bruker D8 Advance X-ray diffractometer with a Ni-filtered $\text{Cu } K\alpha$ ($\lambda = 0.15406$ nm) radiation source at 40 kV and 40 mA. Scans were made in the range of $5^\circ - 80^\circ$ at a rate of $0.04^\circ \text{ deg s}^{-1}$.

2.3. EPR Characterization

The samples (LiMnO_x , NaMnO_x , CsMnO_x , CaMnO_x and MgMnO_x) for EPR characterization were prepared using the same electrodeposition procedure as above, except on a larger FTO electrode (area = 10×12 cm). The prepared film was washed at least six times using purified water in order to wash away any free Mn^{2+} ion on the surface of electrode that remained from the electrolyte solution. The washed film was then air-dried at room temperature and scraped from the electrode surface using a razor blade, yielding ~ 7 mg of dark brown powder. This separated powder was loaded into a Q-band EPR tube (Vitrocom CV2024 ID = 2.0mm OD = 2.4mm L = 100mm), flame-sealed immediately and stored at room temperature.

X-band continuous wave (CW)-EPR spectra were recorded using a Bruker (Billerica, MA) Biospin EleXsys E500 spectrometer with a super-high Q resonator (ER4122SHQE). Cryogenic temperatures (30 and 70 K) were achieved and controlled by an Oxford Instrument ESR900 liquid-helium cryostat in conjunction with an Oxford Instrument ITC503 temperature and gas-flow controller. All CW-EPR data were acquired under non-saturating conditions, with an excitation microwave frequency = 9.39 GHz, microwave power = 0.6325 mW, modulation amplitude = 8 G, and modulation frequency = 100 kHz.

2.4. Electrolysis

Electrolysis for the water-oxidation reaction was conducted at 23 °C in an airtight glass reactor with a three-electrode system. An FTO electrode (area = 1×2 cm) that had been coated with the manganese-oxide film (area = 1×1 cm) was placed in the middle of the reactor to serve as a working electrode, with nickel foam as the counter electrode and Ag/AgCl (saturated with NaCl) as a reference electrode. The distance between the reference electrode and working electrode was no more than 2 mm in order to reduce the solution resistance (iR). The electrolytes were 0.5 M MCl ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Mg}$ or Ca) all in a Tris-buffered solution (pH = 7.8). Electrolysis was started after bubbling argon gas through each solution for at least 1 h before measurement in order to displace any atmospheric O_2 from the system.

Table 1. Properties of water-oxidation catalysts from selected studies.

Catalysts	BET Surface area (m ² ·g ⁻¹)	Particle Size	Valence of Mn Species	TOF (mmol O ₂ ·mol Mn ⁻¹ ·s ⁻¹)	TOF (TOF (per surface area of 1 mol MnO ₂ × number of Mn ions in one mole oxide) × 10 ⁵)	Reference
CaMn ₂ O ₄ ·4H ₂ O	303	5 – 50 μm	Mn(IV)/20% Mn(II)	0.325	74	[50]
CaMn ₂ O ₄ ·H ₂ O	205			0.540	23	
CaMn ₂ O ₄	2.62			0.024	Trace	
α-Mn ₂ O ₃	16.6			0.027	21	
CaMn ₂ O ₄ ·H ₂ O (Concentrated KOH used)	-	< 50 nm	-	2.0	-	[51]
A soluble homogenous form of Mn Oxide colloid (KMnO ₄ + Na ₂ S ₂ O ₃)	-	-	-	5.28	-	[52]
CaMn ₃ O ₈	2.53	Nanorod	3.33	0.046	182	[53]
CaMn ₄ O ₈	2.66	520nm × 65 nm	3.5	0.035	136	
CaMnO ₃	2.54	100 – 150 nm	IV	0.012	37	[54]
CaMn ₃ O ₈	3.47	~ 600 nm	IV	0.016	33	
MnZnOx	-	~ 200 nm	-	1.1	-	[55]
MnAlOx				1.1		
5.64 wt% MnO _x /Zeolites	129	-	-	2.62	-	[56]
α-Mn ₂ O ₃ + amorphous MnO ₂	33.49	~ 100 nm	III/IV	0.15	-	[57]
Hollandite	-	1μm × 5μm × 50μm		0.068	-	[58]
Hausmannite				0.012		
PSII(OEC)	-	0.5nm × 0.25nm × 0.25nm	III/IV	25000	-	[61]

Current (j) vs Potential (U) curves were obtained from linear-sweep voltammetry (LSV) recorded from 0 to 2.0 V vs Ag/AgCl (in saturate NaCl solution) at 1 mV/s with regular stirring (without iR compensation). The amount of O_2 evolved was monitored independently and simultaneously via the current and by using a fluorescence-based oxygen sensor (NeoFox Phase Measurement System with a FOXY-T1000-TS-NEO probe, Ocean Optics, Dunedin, FL, USA), which was placed in front of the working electrode.

3. Results and Discussion

3.1. Manganese-Oxide Film

Figure 1 shows typical X-ray diffraction patterns of manganese oxide after electrolytic deposition in the presence of Li^+ , Na^+ , or Ca^{2+} . Diffraction peaks are evident at $2\theta = 11.84^\circ \sim 12.01^\circ$, and 24.7° and assigned to characteristic (001) and (002) planes of a typical birnessite-type layer-by-layer structure, with (100) plane diffraction at $2\theta = 36.5^\circ$ (36, 68). These XRD results are consistent with previous work by Jaramillo et al. (36), and the resulting materials consist of birnessite-type manganese oxides, with layers of edging-sharing octahedral MnO_6 and with counterions and water molecules occupying the interlayer space. According to Sposito et al. (69), synthetic birnessites tend to have triclinic defects resulting from the substitution of Mn(IV) with Mn(III), which generate negative charges in the layer that must be compensated by the counterions. Therefore, cations with different radii and charges could result in different interlayer distance d_{001} values and could stabilize different concentrations of Mn(III) in the manganese-oxide layers by presenting varying average oxidation state of manganese. As shown in Table 2, the interlayer distance d_{001} values of 7.46 Å, 7.36 Å and 7.46 Å determined in this study for $LiMnO_x$, $NaMnO_x$ and $CaMnO_x$, respectively, are broadly similar to previously reported values obtained for $LiMnO_x$, $KMnO_x$, $RbMnO_x$, and $CsMnO_x$ of 7.2 Å, 7.2 Å, 7.3 Å and 7.5 Å, respectively (70). The d_{001} value increases predictably with the radius of interlayer cation (60, 70). However, in our samples, d_{001} for $LiMnO_x$ is slightly larger than that found for the $NaMnO_x$ sample, which could be due to the fact that the $LiMnO_x$ is not as well-crystallized as the other materials shown in Figure 1.

Cations also affect the average oxidation states of manganese in the layer. In general, one expects the concentration of Mn(III) to vary with the equivalents of counterion charge in the interlayer. Matsui et al. (71) reported the average oxidation state of manganese in similar materials by measuring the ratio of Na^+ to manganese in the solid using ICP analysis, since the concentration of Na^+ should be equal to that of Mn(III) in the layer. In their samples, the ratio of Mn(III) to Mn(IV) was 0.28:0.72 (71) calculating the average oxidation state of manganese to be 3.72. X-ray photoelectron spectroscopy has also been employed to determine the average oxidation state of manganese and shown to fall into the range of 3.6 – 3.7 for birnessite-type manganese oxides similar to those we produced electrolytically (72).

Figure 1. Powder X-ray Diffraction patterns of manganese oxides (LiMnO_x , NaMnO_x and CaMnO_x) prepared by electrolytic-deposition.

For our materials, CW-EPR spectroscopy was employed to characterize the electronic structure of manganese species in the layer. Figure 2 presents X-band CW-EPR spectra of manganese oxide films with divalent alkaline-earth cations (Ca^{2+} or Mg^{2+}) and monovalent alkaline cation (Li^+ , Na^+ or Cs^+) in the interlayer. The spectra were collected at 70 K and 30 K. Samples with interlayer divalent cations exhibit markedly different spectra than samples with monovalent cations, indicating that substitution of these cations is coupled directly to the electronic structure of manganese in the metal-oxide layers, as was expected.

For both Ca- and Mg-bearing samples, broad EPR signals are observed at 70 K with a peak-to-peak spectral width ($\Delta B_{\text{p-p}}$) of ca. 4620 G. However, no obvious signals are detected in spectra acquired at 30 K. This temperature dependence to the signals is consistent with previous EPR studies on manganese oxides that contained Ca^{2+} (73, 74). The interpretation is that significant exchange coupling between Mn(III) and Mn(IV) occurs in the manganese-oxide layers of CaMnO_x and MgMnO_x at 70 K. At much lower temperatures, the spins are $S = 1/2$ Mn(III,IV) dimeric units are antiferromagnetically coupled with other nearby mixed-valent dimers with the extent of coupling dependent upon the separation distance of Mn(III) (ca. $< 2.8 \text{ \AA}$) (73).

Table 2. $d_{(001)}$ and overpotential needed for oxygen evolution for manganese oxides with different intercalating cations.

<i>Cation</i>	<i>Radius ($\text{\AA}$)</i>	<i>$d_{(001)}$ ($\text{\AA}$) in this work</i>	<i>$d_{(001)}$ ($\text{\AA}$) in reference</i>	<i>Overpotential (mV) in pH = 7.8</i>
Li ⁺	0.60	7.46	7.2, (70)	430±75
Na ⁺	0.95	7.36	7.2, (70)	550±75
K ⁺	1.33	-	7.2, (70)	680±75
Rb ⁺	1.48	-	7.3, (70)	740±75
Cs ⁺	1.69	-	7.5, (70)	770±75
Mg ²⁺	0.65	-	7.2, (60)	630±75
Ca ²⁺	0.99	7.46	7.1, (60)	740±75

Samples that were prepared with monovalent cations (LiMnO_x, NaMnO_x and CsMnO_x), exhibited EPR spectra with a narrower signal centered at $g = 2.0$ with ΔB_{p-p} ca. 560 G. We attribute this signal to $S = 5/2$ Mn²⁺-containing-species. Although, no ⁵⁵Mn hyperfine splitting is apparent, the 560 G spectral width is consistent with the 88-95 G magnitude for ⁵⁵Mn hyperfine typically observed for Mn²⁺ species (74). This assignment to a Mn²⁺ species is also consistent with the observed temperature dependence: intensity for the narrow signal decreases as the temperature is increased from 30 K to 70 K (Figure 2). The Mn²⁺ could have originated as an adsorbate metal from the electrolyte solution, but more likely originated as the product of disproportionation of unstable Mn(III) in the manganese-oxide layers. The central observation, however, is that Mn(III) species are more evident in the manganese-oxide material when the interlayer cation is divalent (Ca²⁺ or Mg²⁺), which could resulting in higher concentration of Mn(III) species.

3.2. O₂ Evolution

Sets of manganese oxides were employed as electrocatalysts for the water-oxidation reaction in Tris-buffered solutions (pH = 7.8) with the current-potential (j - U) curves shown in Figure 3. These measurements were collected via LSV at 1 mV/s scanning rate without iR compensation. It should be mentioned that by using a small FTO electrode (area = 1×2 cm), the measured uncompensated resistance was ~12.5 Ω , with iR corresponding to <12.5 mV. The resulting uncompensated current was no more than 1 mA, which will not affect our comparison.

Figure 2. X-band CW-EPR spectra of manganese oxide with both divalent alkaline-earth cation (Ca^{2+} or Mg^{2+}) and monovalent alkaline cation (Li^+ , Na^+ or Cs^+) at 70 K (A) and 30 K (B). The samples were analyzed with parameters of power 0.6325 mW (no saturation), microwave frequency: 9.39 GHz, conversion time: 40 ms, modulation amplitude: 8 G, modulation frequency: 100 kHz.

Figure 3. Current density (j : mA cm^{-2}) of manganese oxides with monovalent alkaline cations (A) and divalent alkaline-earth cations (B) in the corresponding 0.5 M MCl ($M = \text{Li, Na, K, Rb, Cs, Mg or Ca}$) tris-buffer solution ($\text{pH} = 7.8$) during the positive potential linear sweep at scanning rate of 1 mV/s . $E^\circ(\text{O}_2/\text{H}_2\text{O})$ reflects to the standard potential for O_2 evolution.

For manganese-oxide solids with Li^+ , Na^+ , K^+ , Rb^+ or Cs^+ as the interlayer cation, the onset potentials for O_2 evolution are: 1.20 V, 1.32 V, 1.45 V, 1.51 V and 1.54 V (vs NHE), respectively (Figure 3A), with uncertainties within ± 0.02 V. These values corresponds to an overpotential (η) of ca. 430 mV, 550 mV, 680 mV, 740 mV, and 770 mV (with uncertainties within ± 20 mV), respectively, since the standard potential for O_2 evolution at this pH condition is 0.77 V. These overpotentials are comparable to those reported by other researchers for pH-neutral solutions and similar conditions (39). This trend of increasing overpotential with increasing cation size parallels the increase in the electrostatic potential value, as shown in Figure 4. We can only speculate about the cause of this trend of oxidation catalysis with intercalating cation, since the stability Mn(III) species in the layer revealed from EPR (Figure 2) is similar. The difference of intercalating monovalent alkaline cations in radius, electrostatic potential as well as Lewis acidity could contribute to this trend.

Manganese-oxide solids with alkaline-earth cations (Mg^{2+} or Ca^{2+}) exhibit higher overpotentials (ca. 630 and 740 mV ± 20 mV, respectively; Figure 3B) than the lighter alkali metals, Li^+ and Na^+ , that have similar affects on the spacing of layers. The interlayer distance, d_{001} , for CaMnO_x is same to that of LiMnO_x and Lewis acidity of both Ca^{2+} and Mg^{2+} is higher than Li^+ . If Lewis acidity alone was important, one would expect that the electrochemical behavior of electrocatalysts with these alkaline-earth cations to be comparable to that of samples with Li^+ and Na^+ .

In this case, the lower activity must reflect differences in electronic structures of Mn species in the oxide layer (Figure 2). Mn(III) species in manganese oxide layers with alkaline-earth cations (Ca^{2+} or Mg^{2+}) are more stable than samples with alkaline cations (Li^+ , Na^+ or Cs^+). We speculate that the divalent cations may affect the localization of layer charge in the MnO_2 solids, enabling the metal-oxide layers to sustain large amounts of Mn(III). However, the stability of Mn(III) species as revealed by EPR could be different from that of the “*in-situ*” working catalyst in contact with the electrolyte, which greatly complicates comparison.

Above all, for our set of as-deposited birnessite-type manganese oxides with both monovalent alkaline (Li^+ , Na^+ , K^+ , Rb^+ or Cs^+) and divalent alkaline-earth cations (Mg^{2+} or Ca^{2+}), the catalytic activity for electronic water oxidation reaction follows the sequence: $\text{Li}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} \sim \text{Rb}^+ > \text{Cs}^+$, which was similar to the activity reported by Dau et al. in water oxidation reaction system using $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ as electron acceptor and synthetic birnessite-type manganese oxides as catalysts (60). Besides, for Ca^{2+} -depleted PSII enzyme that was then reactivated with Ca^{2+} , Sr^{2+} , Mg^{2+} or Na^+ , the activity for water oxidation followed a similar trends of $\text{Ca}^{2+} > \text{Sr}^{2+} \sim \text{Mg}^{2+} > \text{Na}^+$ (75, 76).

In addition, the effect of post heat-treatment of the as-deposited LiMnO_x film on the activity of O_2 evolution reaction was investigated; results are shown in Figure 5. The potential needed for O_2 evolution is 1.20 V, 1.10 V, 1.00 V and 0.99 V (vs NHE, with uncertainties within ± 0.01 V) respectively, for samples before heat treatment, and for those heated to 200, 300, and 500 $^\circ\text{C}$ for 2 h, respectively. These values for the onset of O_2 production from water correspond to an overpotentials of ca. 430 mV, 330 mV, 230 mV and 220 mV, indicating that heat treatment dramatically affects O_2 evolution. Such heat treatment,

of course, would dramatically change the surface/structure of birnessite-type manganese-oxide films and characterization of these changes is underway.

Figure 4. Correlations between overpotential needed for O₂ evolution and radius (A) and electrostatic potential of cation (B). The blue circles are monovalent alkaline cations and the black diamonds are divalent alkaline-earth cations.

Figure 5. Current density (j : mA cm^{-2}) and evolved O_2 concentration for as-deposited LiMnO_x film, and samples with post heat-treated at 200, 300, and 500 $^{\circ}\text{C}$ for 2 h. Positive potential linear sweep at 1 mV/s is in 0.5 M LiCl tris-buffer solution ($\text{pH} = 7.8$)

The evolution of O_2 as detected from fluorescence measurements matches the electrochemistry. Heat-treated samples evolve O_2 to an enhanced degree relative to as-deposited samples and samples heat-treated at low temperatures (200 $^{\circ}\text{C}$). It should also be mentioned that there is an experimental delay of ca. 400 mV before the O_2 sensor can detect evolved O_2 , which defines response time for the sensor in solution.

In summary, as for birnessite-type manganese oxide with intercalating monovalent alkaline cation (Li^+ , Na^+ , K^+ , Rb^+ or Cs^+), the onset potential for anodic O_2 -evolution reaction is lowest for LiMnO_x and follows the trend: $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ and divalent alkaline-earth cations (Mg^{2+} or Ca^{2+}) appear to affect the manganese-oxide layer more than monovalent cations. Heat-treatment of LiMnO_x film also yields dramatically lower onset potential, with η as low as $220 \text{ mV} \pm 10 \text{ mV}$.

4. Conclusions

Birnessite-type manganese oxides can serve as electrocatalysts for water oxidation, with catalytic activities that depend on the intercalating cation. EPR spectra of birnessite samples with divalent cations (Ca^{2+} or Mg^{2+}) and monovalent cations (Li^+ , Na^+ or Cs^+) suggest that Mn(III) species are more stable in divalent-cation-substituted samples. By far, the smallest overpotential needed

to enable water oxidation was found for heat-treated of as-deposited LiMnO_x , suggesting possible changes in both physical and electronic structure.

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