Using nickel manganese oxide catalysts for efficient water oxidation‡

Prashanth W. Menezes, Arindam Indra, Ophir Levy, Kamalakannan Kailasam, Vitaly Gutkin, Johannes Pfrommer and Matthias Driess*

Nickel–manganese oxides with variable Ni : Mn ratios, synthesised from heterobimetallic single-source precursors, turned out to be efficient water oxidation catalysts. They were subjected to oxidant-driven, photo- and electro-catalytic water oxidation showing superior activity and remarkable stability. In addition, a structure–activity relation could be established.

Splitting of water by an efficient catalyst is one of the major aspects of renewable energy research at present. Discovery of such highly active catalysts with scalable, abundant, robust, stable and low-cost materials is a promising solution for the sustainable production of clean energy. Over the years, first-row transition metal oxides, particularly those with manganese oxide based systems have been widely investigated for photophysical and electrochemical reactions, not only due to their economic and environmental benefits but also because of the fact that nature enables solar to chemical energy conversion with a maximum of dispersion of the nickel and manganese on the atomic level, and of the oxidation states of the metals. A while ago, Fukuzumi et al. reported a NiMnO₃ phase toward water oxidation but other Ni : Mn ratios (compositions) of nickel manganese oxides have not been studied as yet. Therefore, we opted for the single-source precursor (SSP) approach to gain access to a new class of heterobimetallic nickel manganese oxides versus nickel oxide as promising catalysts for efficient oxidant-driven, photo- and electro-catalytic water oxidation.

First of all, nickel manganese and nickel oxalate SSPs were prepared in micro-emulsions containing cetyltrimethylammonium bromide (CTAB) as a surfactant, 1-hexanol as co-surfactant and hexane as the lipophilic phase and mixed with aqueous solution containing Ni²⁺, Mn²⁺ and oxalate ions with tuneable ratios. The thus yielded oxalate SSPs were treated thermally in the presence of dioxygen to form the respective oxide phases of various morphologies. (see ESI,‡ synthesis). The latter method is a reliable way to access these low-cost materials in multimgram-scale quantities.

All precursors were characterised extensively by state-of-the-art techniques and the corresponding data are given in Fig. S1–S9 and Tables S1 and S2 (ESI†), respectively. The thermal degradation of the different heterobimetallic NiMn and homometallic Ni precursors in the presence of dioxygen produced the pure oxides phases NiₓMn₁₋ₓOₓ (JCPDS 42-479), MnNiO₄ (JCPDS 36-83), NiMn₂O₄ (JCPDS 1-1110) and NiO (JCPDS 71-1179), respectively, as confirmed by Powder X-Ray Diffraction (PXRD) analysis (Fig. S10, ESI†). The chemical composition, quantification of Ni : Mn ratio and their presence in the phase was obtained by Inductively Coupled Plasma (ICP) Atomic Emission Spectroscopy (AES) and Energy Dispersive X-ray (EDX) analysis (Fig. S11 and Table S3, ESI†). Interestingly, just by tuning the nickel and manganese ratio, various morphologies have been realised. As shown in Fig. 1, the higher magnification Scanning Electron Microscopy (SEM) images of NiₓMn₁₋ₓOₓ showed a flower-type morphology (~1 μm) which consisted petals assembled from...
nanoparticles and MnNi₂O₄ displayed cubic type particles. NiMnO₄ forms small nanochains whereas NiO exhibits bricks (~400 nm) built of tiny nanoparticles (see also Fig. S12, ESIF). Further insights on the morphology and particle size were gathered by Transmission Electron Microscopy (TEM) and High Resolution (HR) TEM images (Fig. S13, ESIF). In all cases the particles were well crystalline with particle size of about 2–5 nm for Ni₆MnO₈, ~50 nm for MnNi₂O₄, ~10 nm for NiMn₂O₄ and ~5–10 nm for NiO, respectively. The Fourier Transform Infrared (FTIR) spectrum of all oxides is typical and characteristic for metal oxalates (Fig. S14, ESIF). The highest Brunauer–Emmett–Teller (BET) surface area was displayed for Ni₆MnO₈ (51.9 m² g⁻¹) followed by NiMn₂O₄ (39.6 m² g⁻¹), NiO (30.4 m² g⁻¹), and MnNi₂O₄ (29.3 m² g⁻¹), respectively (Fig. S15, ESIF).

The detailed bonding states of Ni, Mn and O were further characterised by X-ray Photoelectron Spectroscopy (XPS). The XPS core level spectra of Ni₂p₃/2 and Ni₂p₁/₂ for Ni₆MnO₈, NiMn₂O₄ and NiO exhibited peaks at binding energy (BE) of ~854.5 eV and 872.2 eV corresponding to Ni²⁺ while the peaks of NiMn₂O₄ shifted to the higher energy of 856 eV and 873.8 eV which can be assigned as the mixture of Ni²⁺/³⁺ (Fig. S16, ESIF). The Ni₂p spectra of Ni₆MnO₈ and MnNi₂O₄ displayed two major peaks for Mn₂p₁/₂ and Mn₂p₃/2 at BE ~643.5 eV and ~655.0 eV that are consistent Mn⁴⁺ species whereas for NiMn₂O₄, the peak positions were shifted to lower energy of 642.4 eV and 653.9 eV and are characteristic for Mn³⁺ (Fig. S17, ESIF). The O1s spectrum for all oxides exhibited a major O²⁻ peak assignable to bridging oxides with two smaller ones that could be attributed to the surface oxygen, physi- and chemisorbed water at or near the surface and to the hydroxide species (Fig. S18, ESIF).

Oxidant-driven water oxidation experiments (see ESIF for details) were conducted with all catalysts (Fig. S19, ESIF) in deoxygenated aqueous solution of 0.5 M ceric ammonium nitrate (CAN) and the rate of the oxygen evolution was calculated from the slope of the linear fitting for the first 60 s. The Ni₆MnO₈ was found to be extremely active with a maximum rate of 1.41 mmolO₂mol⁻¹s⁻¹ considering both nickel and manganese atoms are active, and was approximately thrice higher than the MnNi₂O₄ (0.52 mmolO₂mol⁻¹s⁻¹). However, for NiMn₂O₄, the rate was far lesser with the value of 0.19 mmolO₂mol⁻¹s⁻¹ and is comparable with the pure NiO (0.15 mmolO₂mol⁻¹s⁻¹). The surface area and the total number of active sites present on the catalyst play a crucial role in water oxidation. Therefore, the correlation of surface area normalised plots is shown in Fig. S20 (ESIF) and follows the same trend as that of total mass activity.

The photo-catalytic water oxidation was performed in a phosphate buffer solution of pH 7 in the presence of [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) as a photosensitisers and S₂O₈²⁻ as two electron acceptor (Scheme S1, ESIF). In a similar trend to the oxidant-driven water oxidation, the highest rate of oxygen evolution was exhibited by the nickel-rich Ni₆MnO₈ with a value of 1.00 mmolO₂mol⁻¹s⁻¹ that was again 1.5 times higher than the other nickel-rich MnNi₂O₄ phase (0.69 mmolO₂mol⁻¹s⁻¹) (Fig. 2). The rate of oxygen evolution for the nickel-diluted NiMn₂O₄ was 0.44 mmolO₂mol⁻¹s⁻¹ while NiO showed only a limited activity (0.07 mmolO₂mol⁻¹s⁻¹). To compare the photo-catalytic activity, the commercial manganese oxides and nickel oxide were measured as standards that again showed that as-synthesised catalysts are highly active and of interest (Fig. S21, ESIF). Surface normalisation discloses that the values for MnNi₂O₄ are superior to Ni₆MnO₈ > NiMn₂O₄ > NiO due to their lower surface area (Fig. S22, ESIF). Comparison of the mass and surface normalised activity with other reported catalysts confirmed that the diluted-manganese oxide based Ni systems produced higher oxygen evolution than most of the known active nickel and manganese based catalysts (Table S4, ESIF).

After the Clark electrode experiments, a set of experiments for longer duration was also carried out separately (see ESIF) and the oxygen gas was collected in the head space of the reaction mixture was quantitatively analysed by a gas chromatograph (GC). A maximum oxygen yield of 0.08 mL h⁻¹ of O₂ was detected for Ni₆MnO₈ and 0.07 mL h⁻¹ for MnNi₂O₄ (Table S5, ESIF). Moreover, it is not enough to have catalysts that are extremely active but one of the indispensable criteria is also to know the rate of the catalyst after the photo-catalytic experiments, and therefore, PXRD and HRTEM investigation were conducted on high performance Ni₆MnO₈ and MnNi₂O₄ catalysts. From PXRD and HRTEM images (Fig. S23, ESIF),
attained at 1.87 V. Similarly, for the MnNi$_2$O$_4$ and NiMn$_2$O$_4$, the anodic current started growing at 1.54 \( \text{V vs. RHE} \) whereas the tetrahedral sites are occupied by Ni$^2+$ and octahedral sites by Mn$^{4+}$ and vacancies.29 The vacancies are ordered and well positioned to support Mn$^{2+}$ ions, more active than Mn$^{3+}$ for NiMn$_2$O$_4$. It has been already well described that the Mn$^{2+}$ ions are the active species at our conditions, which may be considered as rock-salt structure, in contrast to a change in the reaction mechanism but would also be expected if mass or ion transport limitations became significant.27,28 However, from the above electrochemical behaviour, it can be inferred that a higher content of Ni ions in the structure leads to lower Tafel slopes and thus, beneficial electro-catalytical properties.

Furthermore, to test the stability of all catalysts, chronoamperometric experiments were carried out (Fig. S28, ESI†) and the current values for NiO and NiMn$_2$O$_4$ were maintained over the period of 15 hours. In the case of Ni$_6$MnO$_8$, increased current values were achieved demonstrating the exceptional stability of catalysts on a long run. On the other hand, a slight decrease in currents was observed for MnNi$_2$O$_4$.

After the long-term stability tests, the electrodes were further characterised by TEM and CV. HRTEM images of NiO, Ni$_6$MnO$_8$, and MnNi$_2$O$_4$ revealed that an amorphous shell of NiOOH appears on the surface of the catalysts, which has already been well described for the Ni based catalysts (Fig. S29, ESI†). After chronoamperometry, the NiO electrode was subjected to CV attaining a lower overpotential (370 mV at 1 mA cm$^{-2}$) with slightly lower current density, which unveils the impressive nature of the catalyst with prolonged durability (Fig. S30, ESI†).

In addition to the alkaline media, the NiO catalyst was also studied in neutral (pH 7) and slightly basic (pH 9) conditions using phosphate and borate buffers and in KOH solution of pH 11, but only resulting into lower activity (Fig. S31, ESI†). The determined Tafel slope at pH 11 was lower than pH 13 elucidating slower kinetics at lower pH (Fig. S32, ESI†).

Based on the higher activity of nickel-rich manganese oxides for oxidant-driven and photo-catalytic water oxidation (Ni$_6$MnO$_8$ > MnNi$_2$O$_4$ > NiMn$_2$O$_4$ > NiO), and conversely, nickel oxide (NiO > Ni$_6$MnO$_8$ > MnNi$_2$O$_4$ > NiMn$_2$O$_4$) for electrochemical OER, a structure activity relation can be deduced. The crystal structure of Ni$_6$MnO$_8$ is cubic (space group $Fm\bar{3}m$) and may be considered as rock-salt structure where 6/8 of octahedral sites are occupied by Ni$^{2+}$ atoms and 1/8 by Mn$^{4+}$ atoms, and by vacancies.29 The vacancies are ordered in the alternative (111) planes (Fig. 4a). Under oxidant-driven and photochemical conditions, not only the Ni$_6$MnO$_8$ provides more active sites due to the presence of higher number of Ni$^{2+}$ as active centres that are supported and stabilised by Mn$^{4+}$ but also an additional (extra) hole density drives this reaction efficiently. However, both MnNi$_2$O$_4$ and NiMn$_2$O$_4$ crystallise in cubic (space group $Fd\bar{3}m$) system and belong to the spinel type (AB$_2$O$_4$) structure (Fig. 4b).30,31 The Mn$^{4+}$ ions occupy the tetrahedral sites and the octahedral sites are preferred by Ni$^{2+}$ for MnNi$_2$O$_4$ whereas the tetrahedral sites are occupied by Ni$^{2+}$ and octahedral by Mn$^{4+}$ for NiMn$_2$O$_4$. It has been already well described that the octahedral sites in a spinel structure play a prominent role than that of tetrahedral sites for water oxidation making Ni$^{2+}$ more active than Mn$^{4+}$ and that itself explains the higher activity of MnNi$_2$O$_4$ in comparison to the NiMn$_2$O$_4$.32,33 The NiO (cubic $Fm\bar{3}m$) adopts a rock-salt structure similar to Ni$_6$MnO$_8$ (Fig. 4c) with octahedral Ni$^{2+}$ and $O^{2-}$, and perhaps because of unavailable support of manganese, displays limited activity.
The situation is partly reversed in the electrochemical water oxidation. The NiO exhibits highest activity followed by nickel manganese oxides. This is due to a large amount of amorphous NiOOH, where Ni\(^{3+}\) is hexa-coordinated (Fig. 4d),\(^{16,23,25}\) is formed on the surface of the electrodes (as shown by TEM and XPS) under electrochemical conditions and the resulting amorphous phase is known to be active for water oxidation by making the system very efficient and has been already well established for other nickel oxide and hydroxides.\(^{16,23,25}\) Interestingly, for \(\text{Ni}_6\text{MnO}_8\), MnNi\(_2\)O\(_4\), and NiMn\(_2\)O\(_4\) lesser amount of NiOOH is generated depending on the amount of nickel present in the catalysts. Therefore, it can be concluded that for oxidant-driven and photo-catalytic water oxidation \(\text{Ni}_6\text{MnO}_8\) is efficient due to higher amount of Ni active sites stabilised by manganese and higher structural-hole density whereas amorphous NiOOH seems to be crucial for electro-catalytic water oxidation due to its structural features.

In conclusion, we investigated for the first time, the oxidant-driven, photochemical and electrochemical water oxidation employing nickel manganese oxide-based catalysts (\(\text{Ni}_6\text{MnO}_8\), MnNi\(_2\)O\(_4\), and NiMn\(_2\)O\(_4\)) with various Ni : Mn ratios and morphologies, starting from well-defined heterobimetallic nickel manganese SSs; their activities were compared with NiO. Nickel-rich manganese oxides were found to be highly efficient with very high activity for oxidant-driven and photo-catalytic water oxidation whereas NiO exhibited higher performance and remarkable stability for electro-catalytic water oxidation. Based on the crystallographic aspects, a structure-activity relationship could be deduced from structural features of the oxide systems. The latter relationship deduced here can help to predesign new material to boost efficiency of water oxidation.

Financial support by the BMBF (L2H project) and the DFG (Cluster of Excellence UniCat) is gratefully acknowledged. O. Levy would like to thank Einstein Foundation Berlin for the financial support and Prof. David Avnir for the helpful discussions.

Notes and references