Electrochemical Water Oxidation by MnO_x/CFP: a Volume Catalyst with High Activity over a wide pH range

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Abstract: Layered manganese oxides directly formed on high surface carbon materials (MnO_x/CFP) show promising electrocatalytic water oxidation activities, especially in neutral to acidic phosphate buffer electrolyte. Post operando ex-situ characterizations revealed a high corrosion stability of the catalyst system over a wide pH range (pH 1-14).

Keywords: electrocatalysis, manganese oxides, water oxidation.

1. Introduction

The efficient catalysis of the four-electron oxidation of water to molecular oxygen (oxygen evolution reaction, OER) is a central challenge for the development of devices for the conversion of electrical energy, ideally from renewable sources (e.g. photovoltaics or wind turbines), into storable chemical energy (e.g. by electrolysis or so-called “artificial leaves”). Inspired by the composition of the oxygen evolving complex of Photosystem II, the biological catalyst for this reaction, we have investigated different manganese oxides (MnO_x). As potential OER materials, layered manganese-oxides from the birnessite mineral family showed the most promising performance in these studies. [1,2] In the following, we developed a route to directly prepare a layered structured MnO_x on carbon based electrode supports with different degrees of graphitization.[3] In electrocatalytic tests it turned out that electrodes where the metal oxide was grown on sp^2 rich carbon supports with a high intrinsic surface area (like carbon fiber paper, CFP) exhibited the highest catalytic rates.

In this study, the electrocatalytic performance of such MnO_x/CFP-anodes was tested under different electrolyte conditions with a special focus on the influence of the pH on activity and stability. Additionally, the MnO_x/CFP-electrodes were further characterized before and after electrolysis by means of XRD, SEM/EDX, ATR-IR- and Raman spectroscopy.

2. Experimental

The preparation route of MnO_x/CFP was based on an in-situ redox reaction between $KMnO_4$ and carbon using a modified redox deposition approach.[3,4] CFP supports were dipped into a stirred solution containing permanganate (0.1 M) and HNO_3 (0.5 M, pH ˜0.4). After the functionalization, the electrodes were annealed in air at 400 °C for 1 h.

The following electrochemical measurements were carried out in a typical three-electrode setup using a BioLogic VSP potentiostat, a Ag/AgCl-reference and a Pt counter electrode. The MnO_x/CFP served as working electrode and measurements were conducted at ambient temperature and under different electrolyte conditions (potassium phosphate solutions, KP_i; pH 1-14).

3. Results and discussion

The electrocatalytic water oxidation abilities of MnO_x/CFP in 1 M KP_i-solution at different pH values (pH 2.5/7/12) were analyzed using several electrochemical techniques. Fig. 1a shows cyclic voltammograms (CV) in the potential range from 1.2-2.0 V vs. RHE. Two distinct regions are observed in the CVs: 1) between 1.2 and 1.6 V a broad, unresolved pseudo-capacitive redox wave is discernible due to the charging of the electrical double layer;[5] 2) above a potential of ˜1.6 V an irreversible oxidation peak appears indicating the onset of the water oxidation. This OER onset shifts from higher values for pH 2.5 (η = ˜370 mV) and 7 (η = ˜350 mV) to lower values for pH 12 (η = ˜300 mV). Additionally, higher current densities and thus higher catalytic rates are observed at higher pH values demonstrating, as shown in several studies before,[6] that water oxidation by transition-metal based catalysts is favoured under basic conditions. The same activity trend is visible in Tafel-plots (Fig. 1b): Tafel slopes of app. 135 (pH 2.5), 110 (pH 7) and 50 mV dec^{-1} (pH 12) reveal faster electron kinetics at higher pH values. Consequently, current densities of 1 mA cm^{-2} are reached at lower overpotentials under alkaline conditions (360 mV) than in neutral (440 mV) or acidic media (465 mV).

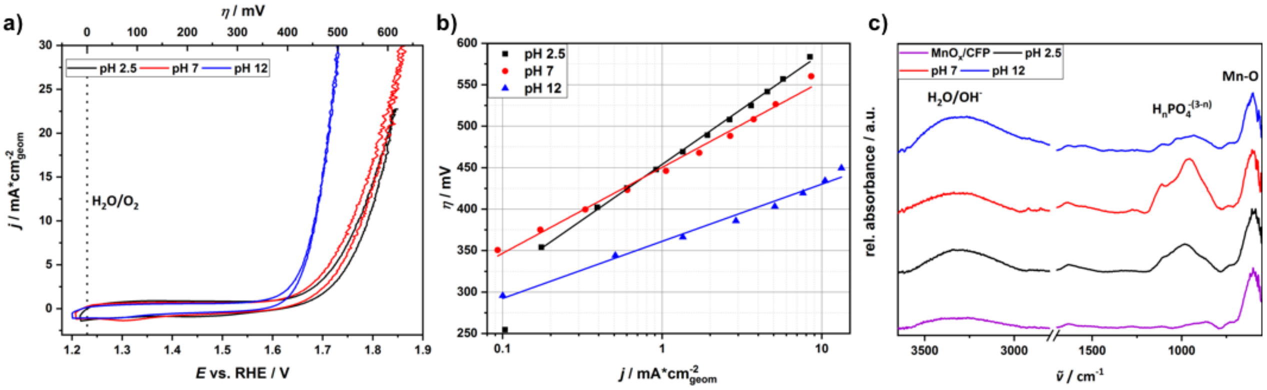

Figure 1. a) CVs for MnO_x/CFP-electrodes tested in 1 M KP_i-buffer at pH 2.5/7/12 (in each case the 3rd cycle is shown); b) Tafel-plots of MnO_x/CFP-electrodes tested under identical conditions showing a linear log j vs. η relationship over two orders of magnitude of current density and extracted from stepwise chronoamperometry experiments; c) ATR-IR-spectra in the spectral range from 4000-550 cm^{-1} of an as prepared MnO_x/CFP-electrode and electrodes treated for 24 h at a constant current density of 2 mA cm^{-2} in 1 M KP_i-buffer at pH 2.5, pH 7 and pH 12, respectively.

In order to determine structural or morphological changes during catalysis, ex-situ post operando studies were carried out. ATR-IR-spectra of samples operated for 24 h at a constant current density of 2 mA cm^{-2} under different pH conditions show, beside the typical absorptions for MnO_x and H_2O,[7] absorptions attributable to in cooperated phosphate ions[8] revealing that $H_nPO_4^{-(3-n)}$ can act as proton-accepting species in the layered structure of the catalyst.

4. Conclusions

In this study we present a catalyst system exclusively based on the abundant elements Mn, O and C showing promising OER activities over the whole pH range. Especially the behavior of MnO_x/CFP-electrodes at pH 2.5 is surprising, since the overall performance, even though lower than under alkaline conditions, is very good compared to other noble metal free catalyst systems.[9,10]

The presentation will include further details on preparation, characterization, electrocatalytic performance and corrosion stability especially under different pH conditions of such MnO_x/CFP-electrodes. Additionally, possible reasons for the different behavior of the electrocatalyst under these conditions will be addressed.

References

1. Frey, C.E., Kurz, Ph., Chem. Eur. J., 2015, 21.
2. Lee, S.Y., González-Flores, D., Ohms, J., Trost, T., Dau, H., Zaharieva, I., Kurz, Ph., ChemSusChem, 2014, 7.
3. Melder, J., Kwong, W.-L., Shevela, D., Messinger, J., Kurz, Ph., ChemSusChem, 2017, 10.
4. Wu, M., Snook, G., Chen, G. Z., Fray, D. J., Electrochem. Comm., 2004, 6, 499–504
5. Zaharieva, I., Chernev, P., Risch, M., Klingan, K., Kohlhoff, M., Fischer, A., Dau, H., Energy Environ. Sci. 2012, 5, 7081.
6. McCrory, C. C. L., Jung, S., Ferrer, I. M., Chatman, S., Peters, J. C., Jaramillo, T. F., J. Am. Chem. Soc. 2015, 137, 4347-4357.
7. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds Part A : Theory and Applications, John Wiley & Sons, New Jersey, 2009.
8. Frost, R. L., Xi, Y., Scholz, R., López, A., Belotti, F. M. Vib. Spectrosc. 2013, 66, 69–75.
9. Huynh, M., Bediako, D. K., Nocera, D. G., J. Am. Chem. Soc., 2014, 136, 6002–6010.
10. Han, L., Tang, P., Reyes-Carmona, Á., Rodríguez-García, B., Torréns, M., Morante, J. R., Arbiol, J., Galan-Mascaros, J. R., J. Am. Chem. Soc. 2016, 138, 16037–16045.