

## Calcium Manganese Oxides as Biomimetic Water-Oxidation Catalysts

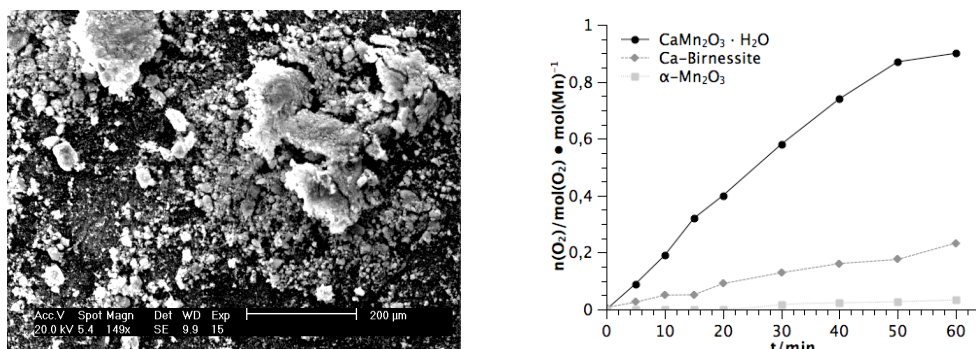
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The amount of solar energy reaching the earth by far exceeds human energy needs. But to take advantage of this enormous potential energy source, concepts and methods have to be developed to capture and convert solar power into useful forms of energy. Water splitting into  $O_2$  and  $H_2$  is one of these concepts and enjoys increasing attention.<sup>[1]</sup> Our research is focused on the water oxidation half reaction (eq. 1).



The  $Mn_4O_xCa$  cluster of the Oxygen-Evolving-Complex (OEC) is the active site of water oxidation in natural photosynthesis.<sup>[1]</sup> Inspired by the composition of the OECs active site, we synthesized calcium manganese(III) oxide particles ( $CaMn_2O_4 \cdot H_2O$ , Fig. 1, left) as biomimetic water oxidation catalysts.<sup>[2]</sup>



**Figure 1:** left: SEM image of  $CaMn_2O_3 \cdot H_2O$ . right: oxygen evolution traces recorded for  $CaMn_2O_3 \cdot H_2O$ , Ca-birnessite and  $\alpha-Mn_2O_3$  reacting with  $Ce^{IV}$  as oxidant, in aq. solution (pH $\approx$ 2).

In oxygen evolution experiments using  $Ce^{IV}$  as one electron oxidant,  $CaMn_2O_4 \cdot H_2O$  is showing high catalytic activity in comparison to manganese(III) oxide without calcium ( $\alpha-Mn_2O_3$ , Fig. 1, right). We also prepared synthetic Ca-birnessite, a mineral that might be formulated as  $K_{0.005} \cdot Na_{0.108} \cdot Ca_{0.141} \cdot Mg_{0.0042} \cdot (MgO)_{0.044} \cdot MnO_{1.76} \cdot 0.77H_2O$ .<sup>[3]</sup> Ca-birnessite has a lower percentage of calcium and shows catalytic activity, but this is between the performance of  $CaMn_2O_4 \cdot H_2O$  and  $\alpha-Mn_2O_3$  (Fig. 1, right). We therefore postulate a correlation between catalytic activity respective to water oxidation and the percentage of calcium ions as part of the manganese oxides. Furthermore, we introduce  $CaMn_2O_4 \cdot H_2O$  and Ca-birnessite as a simple model system for the OEC. Calcium is supposed to act as binding and activation site for  $H_2O$ .<sup>[1]</sup> Both functions are as well imaginable in the presented calcium manganese oxides.

### References

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