Development of a copper doped birnessite manganese dioxide cathode for aqueous zinc-ion batteries

Leandro Schepers

Master of Chemical Engineering Technology

Introduction

In the last 15 years the amount of solar and wind energy has increased drastically, and it will stay increasing. Due to the unreliability of these energy systems the use of big capacitors has been proposed. One of these capacitors are rechargeable batteries. At this moment, the most used rechargeable batteries are lithium-ion batteries. However, lithium is becoming more and more rare and therefore expensive. So the use of other battery materials is investigated, one of which is zinc. Zinc batteries look promising but have one major challenge, that is the search for a useable cathode material. Most cathode materials that work for lithium-batteries do not work for zinc batteries, the cheapest that does work is manganese dioxide. But even though in some circumstances zinc/manganese dioxide batteries show reversible behaviour, the low conductivity of manganese dioxide causes negative effects.

Research proposal

Manganese dioxide has of lot of polymorphs. All these different structures have their own capacity. The structure with the most capacity is called δ-manganese dioxide, also referred to as birnessite manganese dioxide. By doping this structure a more conductive cathode material for reversible zinc batteries can be created. Copper is chosen as doping material, mainly for its high conductivity.

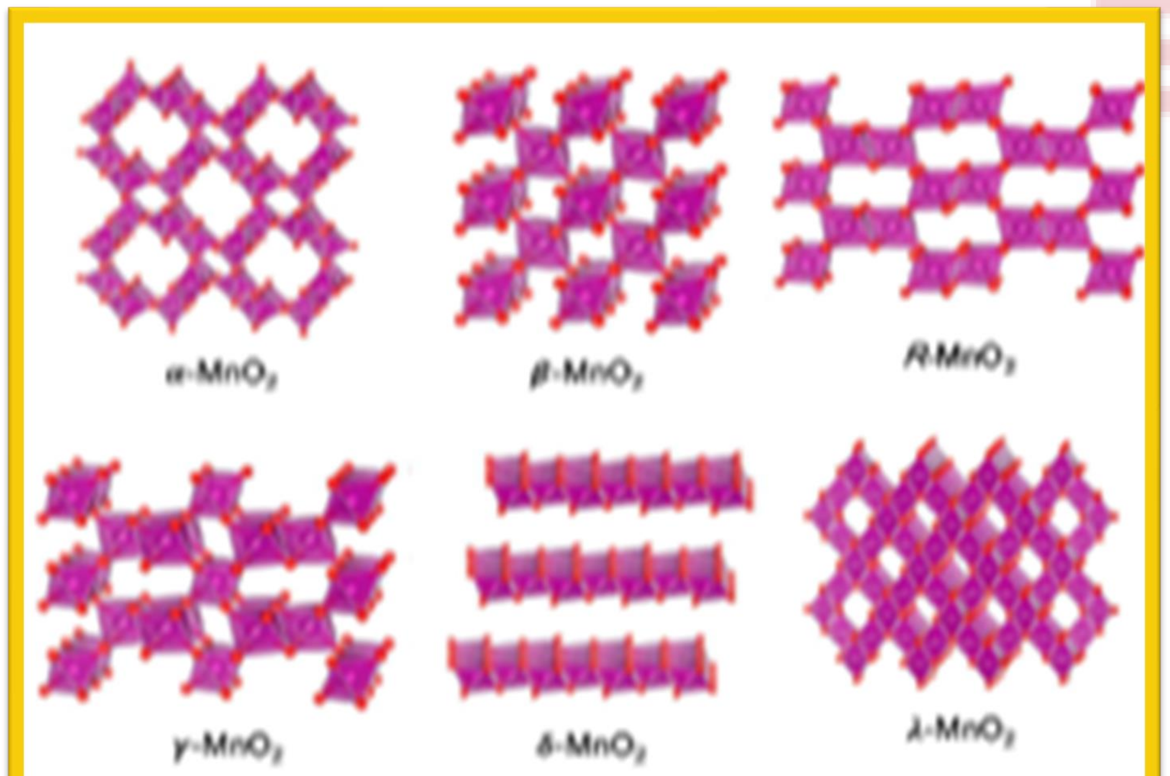

Figure 1. different polymorphs of manganese dioxide

Figure 2. XRD-apparatus (left) and an Autolab to execute cyclic voltammetry and electrochemical impedance spectroscopy (right)

Synthesis

The δ-manganese dioxide is prepared via a chemical precipitation reaction. At first a cold reaction is executed in order to create copper doped poor crystalline δ-manganese dioxide. In a second step the crystallinity is risen via a high temperature/high pressure reaction. Afterwards an electrochemical cell is constructed out of the formed material. Then the structure is verified via XRD measurements, the cyclability is tested by Cyclic voltammetry and resistance is measured via electrochemical impedance spectroscopy.

Results

In the first place the XRD patterns of the of the synthesized δ-manganese dioxide needs to correspond with published XRD patterns as can be seen in figure 3. Secondly the battery qualities need to improve. The major goal is to raise the conductivity of the cathode material. Wang et al have already given positive insight in the conductivity raising performance of doping [1]. Secondly the rechargeability is tested. Here a downside of using δ-manganese dioxide might present itself, namely the mechanical instability of δ-manganese dioxide. Huang et al have proposed a solution for this by reinforcing the manganese dioxide structure with polyaniline. In a further research stadium it might be advisable to combine the doping method with this structural reinforcement idea.

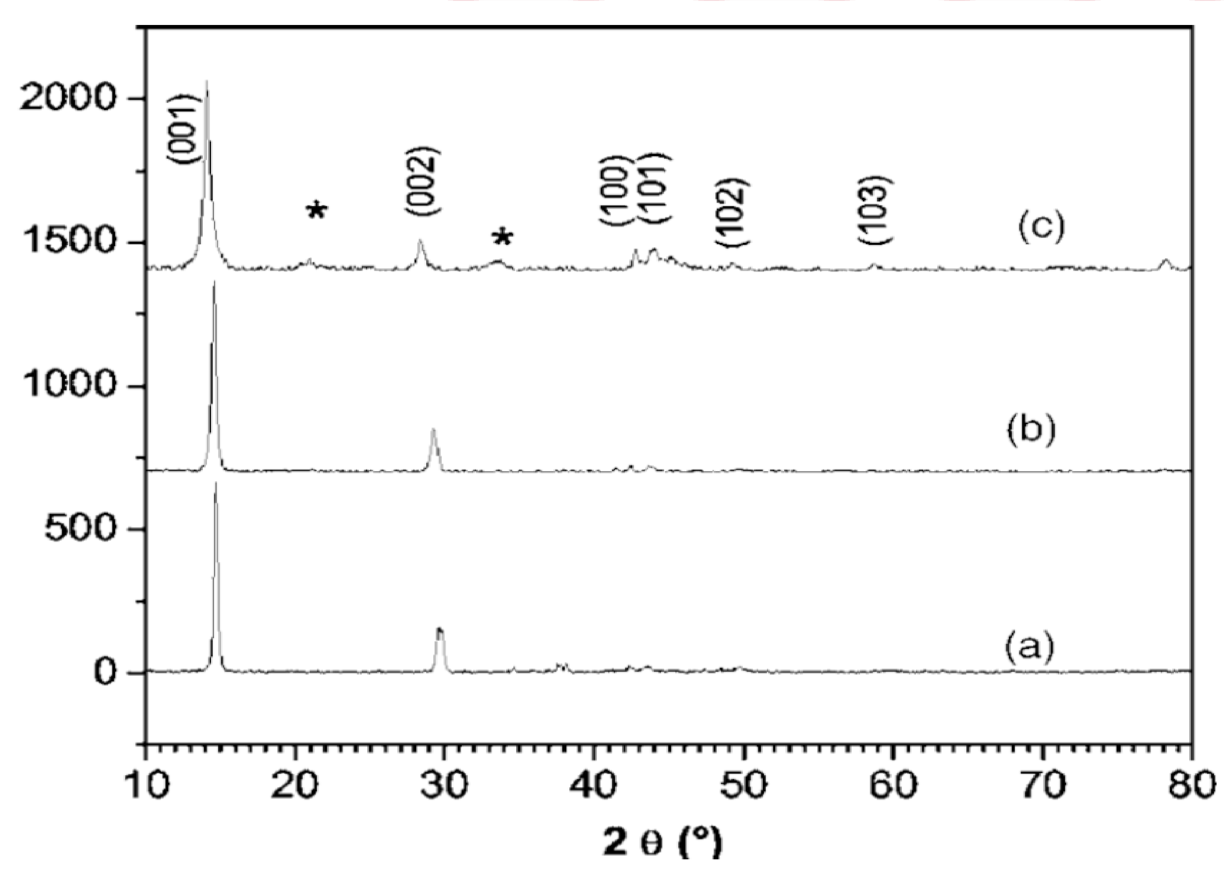

Figure 3. XRD pattern of δ-manganese dioxide

Conclusion

Different sources have reported positive feed-back on the use of transition metals as doping material. However, if the choice for copper has been an optimal one can not be known at this point, since no test have taken place yet. More in general, the status of zinc batteries at this point is that researchers haven't been able yet to produce a useable cathode. The primary reason is the difficulty of finding cathodes that show good cyclability. But secondly if the cyclability is good, the production of these cathodes also needs to be profitable.

Supervisors / Cosupervisors: Prof dr. ir. Leen Braeken
Prof dr. ir. Hoang Thi Bich Thuy
ir. Hang Le Thi Thu

[1] Guiling Wang, Guangjie Shao, Jianping Du, Ying Zhang, Zhipeng Ma," Effect of doping cobalt on the micro-morphology and electrochemical properties of birnessite MnO_2" Materials Chemistry and Physics, vol 138, pp. 108-113, 2013.

TRƯỜNG ĐẠI HỌC BÁCH KHOA HÀ NỘI
HANOI UNIVERSITY OF SCIENCE AND TECHNOLOGY
UHASSELT
KU LEUVEN