

Doctoral (Ph.D.) Theses

# SYNTHESIS AND ENVIRONMENTAL APPLICATIONS OF MANGANESE OXIDES

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Szeged, 2021

# 1 Introduction and aims

Sustainable energy production is the key to the future of humanity as electrical energy demands continue to rise to newer heights, and fossil fuel reserves like natural gas, oil, and coal are slowly diminishing. More than 80 % of the global principal energy source today is fossil fuel-based. Some new studies suggest that humans may consume all discovered reserves of fossil fuels within a few decades, although, future discoveries of fossil fuel reserves might prolong this process. Following the trends of the last century, electrical energy demand is rising exponentially. This growth can be attributed to many factors, like emerging new technologies, increasing automation in agriculture, and the growing global population. Due to these problems, scientists are focusing on finding new sustainable electrical energy production such as renewable energy sources like solar, geothermal, and wind. Considerable research is also being performed to develop fuel cell technologies, to allow for the storage and transportation of the generated energy.

In a fuel cell system, energy is stored chemically. During the release of this energy, two processes take place: oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR). These reactions together produce water from oxygen and hydrogen gas, which are nonspontaneous and require an efficient catalyst. The most common catalysts for the ORR are noble metals such as Pt, Ir, and Ru. These catalysts have high efficiency and stability; however, they also have drawbacks such as high price and rarity in nature. Consequently, significant research is being conducted to find a cheap and environmentally friendly catalyst for ORR.

The burning of fossil fuels emits CO<sub>2</sub> as the main product ranging from 0.5 to 1.1 kg CO<sub>2</sub> for every kWh energy generated. The CO<sub>2</sub> is part of the natural carbon cycle; however, it is a greenhouse gas, and in the last 300 years, the average amount of CO<sub>2</sub> in the Earth's atmosphere increased by a factor of two. The increase of greenhouse gases in the atmosphere can cause health issues, economic crises, and extreme global warming. CO<sub>2</sub> can be captured directly from the air or an industrial source using a variety of technologies. Capturing carbon dioxide from the atmosphere is a promising candidate in next-generation energy source production since valuable fuels (CO, CH<sub>4</sub>, CH<sub>3</sub>OH) can be produced this way and the environmental stress can be reduced as well. Just as for the ORR process, research is underway to identify the stable and cost-effective catalyst for CO<sub>2</sub> hydrogenation.

The imbalance between energy demand and energy production fluctuates in time, thus, an efficient way is needed to store energy when demand is low and use it later when demand is high. Energy storage devices have found applications in many fields. There is a great incentive to replace conventional acid batteries with eco-friendly materials requiring less recharge time, do not utilize hazardous acids, and are abundant in nature. Further research is also underway to manufacture more effective, safe, and long-life cycle energy storage devices such as metal oxide-based supercapacitors.

To find answers to all these questions, manganese (Mn) was selected as the subject of my research, since it is cheap and it is one of the most abundant transition metals (after iron) in the Earth's crust. Due to a wide variety of oxidation states and crystal structures, manganese can have many morphological and physicochemical attributes, therefore, it can be a component for numerous applications. As an environmental chemist, I aimed to find and develop an eco-friendly, cost-effective, safe, simple method for synthesis of nanostructured manganese-based materials, characterize the physicochemical properties, and finally test the synthesized materials for the previously mentioned environmental applications such as oxygen reduction reaction (ORR), CO<sub>2</sub> hydrogenation and supercapacitor:

- I. **To develop the synthesis method of birnessite-like manganese dioxide and test the catalytic activity of the as-synthesized material in the oxygen reduction reaction.**
  - *Developing a synthesis method of birnessite-like manganese dioxide*
  - *Studying physicochemical properties and intercalated ion effects of the initial birnessite and newly developed copper birnessite*
  - *Testing catalytic activity of the potassium birnessite (initial) and copper birnessite for ORR*
  
- II. **To investigate a new method to produce nanosized manganese oxides, which is easy to upscale to allow mass production of the material. Also, to develop a one-pot synthesis method for different metal doping of the same material and compare the results.**
  - *Finding optimum conditions for the synthesis of nanosized manganese oxides by ball milling*
  - *Studying the physicochemical properties of the newly synthesized nano manganese oxide samples*
  - *Testing catalytic activity of the newly synthesized manganese oxides for CO<sub>2</sub> hydrogenation reaction and studying the metal loading (Pt and Cu) and the effect of Pt incorporation into the catalysts*
  
- III. **To investigate a more economical and direct new method for the synthesis of manganese nanostructured materials from natural manganese minerals as precursors instead of synthetic chemicals.**
  - *Developing new synthesis routine of manganese nanosized oxides from the mineral sample*
  - *Studying physicochemical properties of the newly synthesized nano manganese oxide sample*
  - *Testing electrochemical properties as a supercapacitor electrode*

## 2 Applied methods

### *Electrode preparation for oxygen reduction reaction (ORR)*

The surface coating of the glassy carbon electrode (GCE, 3mm diameter, BASi®) was processed by a surface polishing method with an alumina slurry (0.05  $\mu\text{m}$  diameter), then it was rinsed and sonicated with ion-exchanged water and ethanol, then dried. The birnessite sample was mixed with carbon black with a 1:1 weight ratio and was dispersed ultrasonically in a 1:1 V/V ratio mixture of ethanol and water (250  $\mu\text{l}$ ) with an addition of 10  $\mu\text{l}$  of 5 wt% Nafion® to get a homogeneous suspension with the weight concentration of 8.0  $\text{mg}\cdot\text{mL}^{-1}$ . To form a surface-modified glassy carbon electrode, 7.5  $\mu\text{l}$  of this suspension was dropped onto the surface of the pretreated glassy carbon electrode and dried in the air, at room temperature. It corresponds to a catalyst loading of 0.85  $\text{mg cm}^{-2}$  on the geometric area of GCE.

### *Electrochemical oxygen reduction reaction test*

The electrochemical oxygen reduction reaction (ORR) and the durability of the composites were investigated in a three-electrode glass cell using an ACM Instruments GILL AC electrochemical workstation at 23°C. The working electrode was a surface modified glassy carbon electrode (the preparation of which was described above), while Ag/AgCl (3M NaCl, BASi®) and a platinum wire served as reference and counter electrodes, respectively. The voltammetry measurements were carried out in nitrogen- or oxygen-saturated 0.1 M KOH solution. Electrocatalytic activity of the working electrodes was investigated by using cyclic voltammetry (CV) in the potential range between 0 and  $-1\text{V}$  vs Ag/AgCl (3M NaCl) at a scan rate of  $10\text{mVs}^{-1}$ . Linear sweep voltammetry (LSV) measurements with a rotating disk electrode (RDE) were carried out in the same potential range with a rotation rate between 500 and 2500 rpm. The linear sweep voltammograms are depicted and used after background correction. The stabilities of the as-prepared catalysts were measured by the chronoamperometric method. The current retention vs operating time curves were registered to apply a constant potential of 0.4 V (vs RHE) in oxygen-saturated 0.1 M KOH solution at 1500 rpm rotating rate with 10 000 second operation time.

### *Catalytic CO<sub>2</sub> hydrogenation reaction over manganese oxide catalysts*

Before the catalytic experiments, the catalysts were oxidized in the O<sub>2</sub> atmosphere at 300 °C for 30 min to remove the surface contaminants, as well as the PVP capping agent, then reduced in H<sub>2</sub> at 300 °C for 60 min. Catalytic reactions were carried out at atmospheric pressure in a fixed-bed continuous-flow reactor (200 mm long with 8 mm i.d.) and heated externally. The dead volume of the reactor was filled with quartz beads. The operating temperature was controlled with a thermocouple placed inside the oven close to the reactor wall, to assure precise temperature measurement. For catalytic studies, small fragments (about 1 mm) of slightly compressed pellets were used. Typically, the reactor

filling contained 150 mg of catalyst. In the reacting gas mixture, the CO<sub>2</sub>: H<sub>2</sub> molar ratio was 1:4, if not denoted otherwise. The CO<sub>2</sub>: H<sub>2</sub> mixture was fed with the help of mass flow controllers (Aalborg), the total flow rate was 50 ml/min. The reacting gas mixture flow entered and left the reactor through an externally heated tube to avoid condensation. The analysis of the products and reactants was performed with an Agilent 6890 N gas chromatography equipped with a HP-PLOTQ column. The gases were detected simultaneously by thermal conductivity (TC) and flame ionization (FI) detectors. The CO<sub>2</sub> was transformed by a methanizer to methane before analysis with FID.

#### ***Electrochemical electrode preparation for capacitance test (CV, GCD, EIS)***

Electrochemical measurements were performed on the electrochemical station potentiostat/galvanostat instrument (Autolab PGSTAT302N, Metrohm Autolab B.V.) in KOH (0.1M) aqueous solution. The working electrode was a bare carbon paper electrode and MnOx-D/CP, while Ag/AgCl (3M NaCl, BASi®) and a platinum wire served as a reference and counter electrode, respectively. The capacitance of the working electrodes was investigated by using cyclic voltammetry (CV) in the potential range between 0 and -1 V vs Ag/AgCl (3M NaCl) at different scan rates, such as 0.005-0.05 V s<sup>-1</sup>. Specific capacitance retention measured with 2100 cycles of CV. The galvanostatic charge-discharge measurement was carried out with a current density of 0.1 A/g – 2 A/g and a potential limit (cut-off) of 0.5 V. EIS measurement was performed in the frequency range of 10,000 Hz – 0.001Hz.

### 3 Summary of new scientific results

#### A. Publication 1. “Cost-effective ion-tuning of Birnessite structures for efficient ORR electrocatalysts” related thesis points:

***T1. We successfully modified the synthesis of birnessite by longer ageing and additional ion tuning and produced 2 different ions intercalated Birnessites.***

A simple method was developed for the synthesis of large specific surface area birnessite with or without interlayer copper cations. The method resulted in small, nanoparticle-like morphology and significant specific surface area (from 21.6 m<sup>2</sup>/g to 77.8 m<sup>2</sup>/g) as well. Copper cation tuning in the interlayer was proved by the characterization techniques (XRD, RAMAN, TEM, EDS).

***T2. We experimentally proved that ion intercalated birnessite samples have high catalytic activity and excellent electrochemical stability in ORR.***

Both (Birnessite and Cu<sup>2+</sup>/Birnessite) samples were showed good catalytic activity in ORR. Notably, the incorporation of copper ions enhanced the activity of the birnessite structure resulting in an improved electron transfer number (3.6 > 3.4) and higher electrochemical stability during the ORR test (95 > 87 % retention after 10,000-seconds of measurement). It was shown that the oxidation state ratio of Mn<sup>3+</sup>/Mn<sup>4+</sup> in birnessite structure played important role in ORR catalytic activity, and the intercalated copper ion increased the Mn<sup>3+</sup> ratio and stabilized its charge transfer characteristics.

#### B. Publication 2. “One-pot mechanochemical ball milling synthesis of the MnO<sub>x</sub> nanostructures as efficient catalysts for CO<sub>2</sub> hydrogenation reactions” related thesis points:

***T3. We were the first to produce manganese oxides by one-pot mechanochemical synthesis.***

A novel mechanochemical route for the synthesis of nanostructured pure and metal-loaded (Cu, Pt) manganese oxide was demonstrated for the first time. It can be easily scaled up for industrial applications. The shape, porosity, specific surface area, as well as the ratio of the different oxidation states of the Mn-ions in the structure, could be tuned by the milling parameters.

***T4. We found that increased milling speed enhances the catalytic activity of the pure manganese oxide samples for CO<sub>2</sub> hydrogenation reaction.***

The synthesized nanostructured manganese oxides exhibited exceptional performance in the CO<sub>2</sub> hydrogenation reaction. M600 catalysts showed the highest CO<sub>2</sub> consumption rate (~20.000 nmol·g<sup>-1</sup>·s<sup>-1</sup>) followed by M450 (17.500 nmol·g<sup>-1</sup>·s<sup>-1</sup>). Both M600 and M450 were almost two times more active compared to the catalyst milled at 200 rpm (~10.000 nmol·g<sup>-1</sup>·s<sup>-1</sup>) at 873 K. The

high catalytic activity of manganese-oxide milled at higher speeds can be attributed to the high specific surface area and porosity as well as the differences in the crystal structure and oxidation state of the manganese ions.

***T5. Metal doping (Pt and Cu) affects the catalytic activity of the manganese oxides and the amount of improvement depends on the reaction temperature. Specifically, Pt doping could improve catalytic activity significantly at a lower temperature when compared with Cu doping. But at high temperature, Pt and Cu doped samples showed an almost similar result.***

The catalytic activity at 673 K could be significantly enhanced by adding metal into the manganese-oxide structure – ~12-13 and ~2.5 times upon the addition of platinum and copper, respectively. This activity enhancement, however, disappeared at a higher temperature (873 K). This phenomenon shows that temperature plays a vital role in the activity of the manganese oxide-based catalysts due to the oxidation state of the manganese ions (proven by XPS). It also reveals that expensive noble metal platinum can be replaced by copper since they show similar catalytic activity at a higher temperature (873K).

***T6. One-pot synthesized Pt-doped manganese oxide was showed higher catalytic activity and methane selectivity than samples doped Pt by different methods such as wet impregnation or sonication method.***

Pt-doped manganese oxide sample was synthesized using a simple one-pot method and was tested in the CO<sub>2</sub> hydrogenation reaction. The one-pot synthesized Pt/MnO<sub>x</sub> sample showed 30% higher CO<sub>2</sub> consumption rate at 673 K than other manganese oxide samples doped with Pt using different techniques (impregnation or loading of pre-synthesized 5 nm Pt nanoparticles by ultrasonication). Furthermore, it was also found that one-pot synthesized Pt/MnO<sub>x</sub> had 1.5-2 times higher selectivity towards methane than the other samples. Through this observation, the formation of a unique Pt/MnO<sub>x</sub> interface during the milling process was assumed.

**C. Manuscript under publication “A novel synthesis of nano manganese oxide from the mineral and application study for supercapacitor electrode” related thesis points:**

***T7. We investigated a novel synthesis method of manganese oxide electrode from local mineral.***

We have proved for the first time that local mineral pyrolusite (originated from Úrkút, Hungary) could be used directly as a precursor for supercapacitor electrode synthesis. Using a two-step milling process (dry and wet) on the raw material the particle size of the mineral decreased from a few mm to hundreds of nanometers improving the dissolution rate of manganese dioxide under acidic condition (using biodegradable eco-friendly oxalic acid). In the final step electrophoretic

deposition was successfully applied in a two-electrode cell to deposit ~100 nm flower-like nanostructured MnO<sub>x</sub> onto the carbon paper electrode.

***T8. The electrochemical characterization revealed that the mineral-based manganese oxide electrode has high specific capacitance.***

The electrochemical properties of the novel mineral-based nanostructured electrode were studied in a three-electrode cell system. The specific capacitance of the electrode obtained from CV measurement varied between 68-119 F/g, and it depended upon the applied scan rates. The galvanostatic charge-discharge measurement revealed that the prepared manganese oxide electrode had a fast charge-discharge ability, and the specific capacitance ranged between 68-195 F/g at different current densities, which is in good agreement with the results obtained from the CV method. The specific capacitance of our electrode (made without polymer binders or conductive additives) was found to be comparable to MnO<sub>x</sub> analytical reagent electrodes.

## 4 Scientific publications

Hungarian Scientific Bibliography (MTMT) identifier: 10066745

### **Publications that are related to the Ph.D. thesis:**

*Ochirkhuyag Altantuya, Tamás Varga, Ildikó Y. Tóth, Ágnes Tímea Varga, András Sápi, Ákos Kukovecz, Zoltán Kónya*

Cost-effective ion-tuning of Birnessite structures for efficient ORR electrocatalysts, International Journal of Hydrogen Energy, Volume 45, Issue 32, 11 June 2020, Pages 16266-1627 (*Q1, impact factor: 4.939*)

Number of independent citations: 2

*Ochirkhuyag Altantuya, András Sápi, Ákos Szamosvölgyi, Gábor Kozma, Ákos Kukovecz and Zoltán Kónya*

One-pot mechanochemical ball milling synthesis of the MnO<sub>x</sub> nanostructures as efficient catalysts for CO<sub>2</sub> hydrogenation reactions, **Phys. Chem. Chem. Phys.**, 2020, **22**, 13999-14012 (*Q1, impact factor: 3.430*)

Number of independent citations: 2

### **Publication that is not directly related to the Ph.D. thesis:**

*Ochirkhuyag Altantuya, Ildikó Y. Tóth, Attila Kormányos, Csaba Janáky, and Zoltán Kónya*

Composition-Dependent Optical and Photoelectrochemical Behavior of Antimony Oxide Iodides, Journal of the Electrochemical Society, Volume 166, Number 5 (*Q1, impact factor: 3.721*)

Number of independent citations: 1

## **Conference lectures and poster**

### **Lectures:**

*Ochirkhuyag Altantuya, Balázs Buchholz, Ákos Kukovecz, Zoltán Kónya*

“Synthesis and characterization of new antimony-oxide based photocatalysts”, HSM Annual Meeting 2017, Siófok, Hungary

*Ochirkhuyag Altantuya, Tamás Varga, Ildikó Tóth, Zoltán Kónya*

Influence of a dopant on birnessite (manganese oxide) and electrochemical catalytic activity for oxygen reduction reaction (ORR), FEMS Junior EUROMAT conference, 8-12 July 2018, Budapest, Hungary

### **Poster:**

*Ochirkhuyag Altantuya, Tamás Varga, Ildikó Y. Tóth, Ágnes Tímea Varga, Ákos Kukovecz, Zoltán Kónya*

“Influence of an interlayer cation exchange for birnessite and electrochemical activity for oxygen reduction reaction (ORR)”, 8th Szeged International Workshop on Advances in Nanoscience (SIWAN 8), 7 – 10 October 2018, Szeged, Hungary