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Microwave-assisted hydrothermal synthesis of layered manganese dioxide as intercalation material for Al-Ion battery

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Introduction

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- Al – Ion battery is a possible alternative to present Li – Ion technology because of its significantly higher volumetric capacity (8040 mAh / cm³ for Al vs 2046 mAh / cm³ for Li)
- Manganese is a abundant, non toxic and cheap material. Layered δ-MnO_2 allow electrolyte intercalation & deintercalation in 2D direction
- Pore diameter for intercalating electrolyte ions in δ-MnO_2 is ≤4 Å that makes intercalation of $AlCl_4^-$ ions from EMIM-Cl based electrolyte (5.3 – 6.4 Å) challenging
- Common synthesis of δ-MnO_2 e.g hydrothermal, sol-gel or heat induced decomposition of potassium permanganate requires reaction times for at least 24 h

Motivation & Challenges

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1. Microwave-assisted hydrothermal synthesis of layered δ-MnO_2 (Birnessite) should decrease reaction time from ~24 h down to more practicable < 5 h and help to get nanoscale particles
2. Short diffusion path length are needed for intercalation/deintercalation of large $AlCl_4^-$
3. Deposition of dispersed MnO_2 on carbon black should increase capacity and electronic conductivity
4. However, synthesis of favored pure hexagonal phase on carbon wasn't done before and is very challenging

Sample preparation

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1. Dispersing of carbon black in isopropanol / water
2. Molar ratio carbon to MnO_2 (1:4)
3. Adjusting [OH^-] to 1.6 M with KOH
4. Addition of 0.28 M $Mn(NO_3)_2$ solution
5. Addition of 0.09 M $KMnO_4$ solution
6. Microwave-assisted hydrothermal reaction at 110°C

Comproportionation reaction

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Induction period

- Precipitation of $Mn(OH)_2$
- Oxidation of $Mn(OH)_2$ to MnOOH

$$Mn^{2+} + 2\,OH^- \rightarrow Mn(OH)_2$$

$$Mn(OH)_2 + MnO_4^- + OH^- \rightarrow MnOOH + MnO_4^{2-} + H_2O$$

Crystallization period

- Oxidation of MnOOH to δ-MnO_2
- Crystallization

$$2\,MnOOH + MnO_4^{2-} \rightarrow 3\,MnO_2 + 2\,OH^-$$

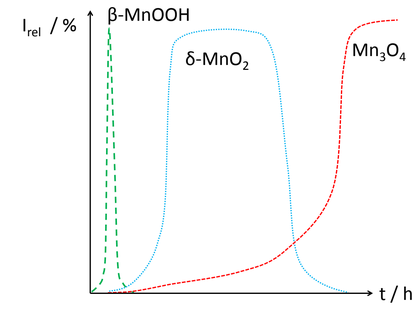

Fig. 1 Assumed reaction process

Morphology of synthesized cathode material

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Molar ratio carbon to MnO_2 (1:4) was fixed because of highest capacity during CV measurements

- In absence of carbon, comproportionation always led to hexagonal δ-MnO_2
- After drying for 24 h at 120°C, monoclinic crystal phase prevailed probably due to thermodynamically favored crystal phase

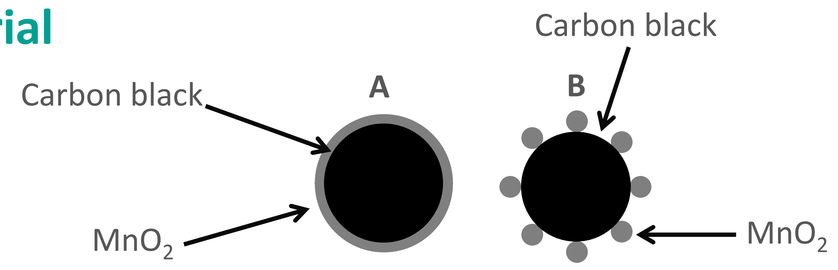

Fig. 2 Different appearances of MnO_2 deposited on carbon (A & B)

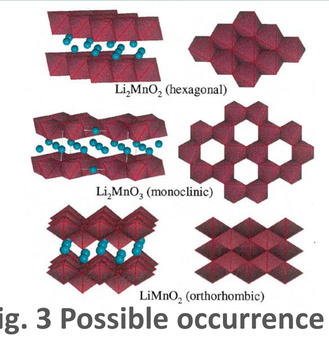

Fig. 3 Possible occurrence of layered MnO_2 crystal phases[4]

XRD analysis

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- Synthesis without carbon (Fig. 4):
  - pure δ-MnO_2 is obtained during 14-96 h reaction time
  - After 96 h reaction time, birnessite phase starts to collapses to spinel phase
- Synthesis with carbon (Fig.5):
  - Formation of δ – MnO_2 occurs after only 1.5 h
  - But spinel (hausmannite) phase was detected as well, and increased with reaction time

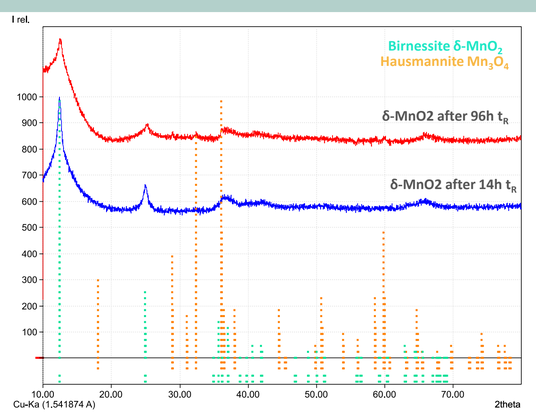

Fig. 4 Influence of reaction time in MW on MnO_2 crystal structure

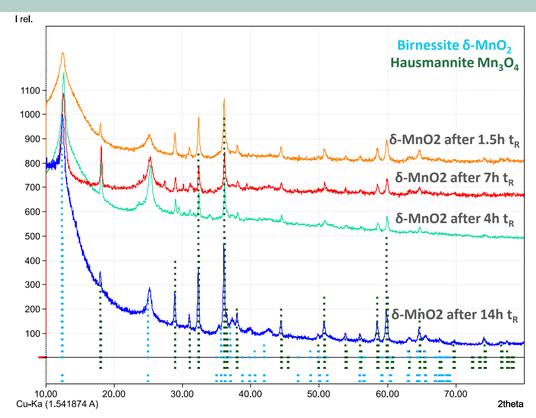

Fig. 5 Influence of reaction time in MW on carbon-supported MnO_2 crystal structure

SEM analysis

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- Highly porous structure
- Very good MnO_2-coated Carbon particle distribution in the range of 80 - 130 nm.
- It seem s that carbon particle are completely covered by MnO_2 as shown in Fig. 2B

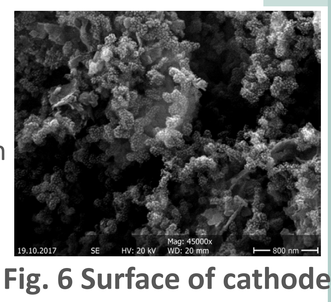

Fig. 6 Surface of cathode material

Conclusion & Outlook

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- Yield of pure δ-MnO_2 only possible in absence of carbon for at least 14 h in MW
- Carbon presence accelerated spinel formation
- Synthesis led apparently to MnO_2/C core-shell structure
- Optimization of synthesis parameters especially reaction temperature to
  - decrease hausmannite formation
  - favor nano-disperse MnO_2 formation on carbon

References

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