

Investigation on electroactive materials for rechargeable aqueous aluminum-metal/ion battery

A thesis submitted in partial fulfillment of the requirements
for award of the degree of
Doctor of Philosophy

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December, 2022

Chapter 7

Conclusion & Future Aspects

7.1. Conclusion

The principal conclusion and pertinent findings from the thesis are outlined in the following chapters:

Chapter 2 (Part I): Rechargeable aqueous aluminum-metal battery with exfoliated graphite as cathode.

1. A facile concept of rechargeable aqueous Al-metal battery with electrochemically pretreated Al and exfoliated graphite foam electrodes is illustrated.
2. The electrochemical pretreatment process resulted in exfoliation of graphite electrode, which is termed as graphite foam. The discharge capacities for the initial and 50th cycles are 213 mAhg⁻¹ and 88 mAhg⁻¹, respectively, at a current density of 0.5 Ag⁻¹.
3. It is found that the lifespan of the investigated Al-graphite cell is limited by the dissolution of the Al electrode during consecutive charge/discharge processes. But, the immense promise of long-term sustainability of the system is shown by mechanical recharge of the Al electrode.
4. The presented aqueous Al-metal battery takes the advantage of raw materials which are locally available in high abundance, low-priced, and ecofriendly. Besides, the ease in handling the materials and assembling the battery system opens exciting opportunities for safe, sustainable, and affordable energy storage device.
5. The possible Al³⁺ ion storage mechanism is also highlighted.

Chapter 2 (Part II): A simple strategy to improve the electrochemical performance of rechargeable aqueous aluminum-metal battery

1. A simple electrochemical and heat treatment method is demonstrated for graphite exfoliation.
2. The heat treatment resulted in formation of nanosized graphite flakes.
3. The exfoliated graphite showed enhanced performance for Al³⁺ ion storage in aqueous electrolyte.
4. A discharge capacity of 100–120 mAhg⁻¹, whereas exfoliated graphite shows only 50–60 mAhg⁻¹ at current rate of 0.5 Ag⁻¹.
5. The enhanced performance is due to lesser charge transfer resistance.

6. The influence of ‘water-in-salt’ electrolyte in the electrochemical performance was also investigated.

Chapter 3 (Part I): Bismuth oxide (Bi₂O₃): A promising electrode material for Al³⁺ ion storage

1. The electrochemistry of Al³⁺ ion insertion in Bi₂O₃ is demonstrated.
2. Exfoliated graphite as a current collector improves the long-term cycling stability.
3. It is found that a binder free integrated electrode of Bi₂O₃ on an exfoliated graphite current collector is needed to improve the electroactivity of Al³⁺ ion storage.
4. The Al metal anode with integrated Bi₂O₃ cathode could delivers a stable Al³⁺ ion storage capacity of 103 mAhg⁻¹ at a current rate of 1.5 Ag⁻¹ over several charge/discharge cycles.
5. It is revealed that an electrochemical conversion reaction of the type Bi₂O₃ + 2Al³⁺ + 6e⁻ → 2Bi + Al₂O₃ occurs during the discharge processes and it was highly reversible.

Chapter 3 (Part II): Bismuth oxychloride (BiOCl): another promising electrode material for Al³⁺ ion storage

1. Reversible Al³⁺ ion storage in BiOCl is illustrated in aqueous electrolyte.
2. It is found that capacity decline was a major concern.
3. A simple and innovative strategy was adopted to dramatically improve the electrochemical stability by synthesizing a binder-free BiOCl electrode on a thermally exfoliated graphite current collector.
4. A stable discharge capacity of 145 mAhg⁻¹ was achieved over 200 cycles at a current rate of 2.5 Ag⁻¹.
5. Based on the ex-situ XRD, FESEM and ex-situ XPS, the Al³⁺ ion storage mechanism is examined.
6. It is found that similar conversion type of electrochemical reaction is possible in BiOCl due to Al³⁺ ion intercalation.
7. Al³⁺ ion storage in bismuth oxyiodide (BiOI) is also highlighted.

Chapter 4: Vanadyl ethylene glycolate (VO(CH₂O)₂): an organic-inorganic hybrid for Al³⁺ ion storage

1. The Al³⁺ ion electrochemistry of vanadyl ethylene glycolate (VEG) in aqueous electrolyte is illustrated.
2. A binder free electrode was processed in carbon cloth substrate.
3. The binder free VEG electrode improves the electrochemical performance for Al³⁺ ion storage in aqueous electrolyte
4. Binder free VEG exhibits excellent cycling stability with specific capacity of 77 mAhg⁻¹ over hundreds of cycles at current rate of 2 Ag⁻¹ whereas pristine form of VEG shows negligible specific capacities (~ 2.3 mAhg⁻¹).
5. The significant improvement in electrochemical performance may be attributed to the intimate electrochemical contact between the electrode and current collector.
6. It is observed that crystalline VEG transform into an amorphous phase after the Al³⁺ ion electrochemical processes.
7. It is found that the diffusion-controlled process is the most dominating process.

Chapter 5: Reversible metal ion (Li⁺, Na⁺, Mg²⁺, Al³⁺) insertion in MoTe₂ for rechargeable aqueous battery

1. The electrochemical activities of MoTe₂ are demonstrated for Li⁺, Na⁺, Mg²⁺, and Al³⁺ ions in aqueous electrolytes.
2. It is observed that Al³⁺ ion intercalation/extraction is possible in MoTe₂ in aqueous electrolyte.
3. It is found that MoTe₂ exhibits superior electrochemical performance for Al³⁺ ion storage than other metal ions.
4. A high discharge specific capacity of 100 mAhg⁻¹ after 250 cycles is achieved for Al³⁺ ion storage at a current rate of 1 Ag⁻¹ with an excellent long term cycling performance (50 mAhg⁻¹ over 2000 cycles at a high current density of 5 Ag⁻¹).
5. It is highlighted that there may be a possibility of crystal phase transition of MoTe₂ to aluminum telluride phase due to Al³⁺ ion intercalation.

6. The polarization is lowest in the case of Al^{3+} ion which is around 0.17 V.

Chapter 6 (Part I): An electrochemical study on lithium manganese oxide (LiMn_2O_4) for Al^{3+} ion storage in aqueous electrolyte

1. The electrochemistry of Al^{3+} ion insertion in LiMn_2O_4 is demonstrated.
2. It is noticed that Al^{3+} ion intercalation process completely destroys the crystal structure of LiMn_2O_4 after first discharge with concomitant rise of a new phase of MnO_2 .
3. Moreover, when tested with reference to an Al anode, LiMn_2O_4 shows an almost flat discharge plateau at 1.5 V with a very low polarization (< 0.4 V).
4. It is found that AlCl_3 aqueous electrolyte is more suitable than $\text{Al}_2(\text{SO}_4)_3$ and $\text{Al}(\text{NO}_3)_3$ aqueous electrolytes.
5. It is revealed that pre-addition of a low-valence Mn salt in the electrolyte further improve the Al^{3+} ion storage capacity.
6. A discharge capacity of 65 mAhg^{-1} could be achieved at a higher current rate of 800 mA g^{-1} at the 75th cycle.
7. The Al- LiMn_2O_4 cell demonstrates remarkably low self-discharge.
8. The Al^{3+} ion storage mechanism is also highlighted.

Chapter 6 (Part II): Reversible Al^{3+} ion storage in lithium manganese phosphate (LiMnPO_4) in aqueous electrolyte

1. Al^{3+} ion insertion in LiMnPO_4 is illustrated.
2. Initially, a very high Al^{3+} ion storage capacity of 146 mAhg^{-1} is observed at a current rate of 1 Ag^{-1} , whereas a discharge capacity of only 28 mAhg^{-1} could be achieved for Li^+ ion.
3. At a higher current rate of 2.5 Ag^{-1} , LiMnPO_4 exhibits a stable specific capacity of 50 mAhg^{-1} over 450 cycles.
4. A rechargeable aqueous Al^{3+} ion cell is demonstrated with LiMnPO_4 as cathode and WO_3 as anode.
5. The $\text{LiMnPO}_4/\text{WO}_3$ cell shows very stable cycling behavior.
6. The assembled cell shows a discharge capacity in the range $27\text{-}30 \text{ mAhg}^{-1}$ over 200 cycles at a current rate of 0.5 Ag^{-1} .

7.2 Future Outlook

Aluminum batteries are still in its early stages and only few potential electrode materials have been introduced in this area. The following points could be considered for further studies in this area.

1. To stop the corrosion of Al metal anode, surface modification of the Al metal could be introduced by in-situ technique.
2. New electrodes such as layered transition metal compounds could be investigated for Al³⁺ ion storage.
3. 3D structured batteries may be created via 3D printing, which may result in greater performance and better space efficiency.
4. Temperature dependent studies are also important.
5. Strategies for achieving flexible aluminum batteries.