Development and optimisation of electrode materials for lithium-ion rechargeable batteries

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Development and Optimisation of Electrode Materials for Lithium-Ion Rechargeable Batteries

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Summary

Lithium-ion battery technology is entering a new era. Demand for not only clean but much advanced materials has overwhelmingly increased. Consumers now have a taste for portable-rechargeable energy and want it featured in all kinds of applications ranging from microelectronics to automobiles. Fulfilling these demands in a sustainable and widespread fashion will require breakthroughs in technology and hence represents an enormous challenge and responsibility for the scientific community.

Nanoscience on the other hand has attracted enormous attention in the last decade, volumes have been written on how the reduced dimensions of a particle can transform its mechanical and electronic properties. This persisting hype has left many restless and wondering how soon will this so called ‘nano-boom’ have an impact on actual products and applications.

Li-ion batteries provide a perfect springboard for directing the versatility of nanoparticles into product development. The future of Li-ion batteries is intractably linked to the development of novel nanosized particles, as the improvement in the electronic conductivity, structural stability and ionic diffusivity of materials is the cornerstone for progress in this field.

The present work focussed on the development and electrode optimisation of cathodic and anodic materials which could be used in the next generation of Li-ion batteries. All of the synthesised and optimised materials are in the micro or nano sized regime, which is a prerequisite for their desired performance.

In the first chapter, the synthesis of nanoscopic LiFePO₄ using optimised hydrothermal and polyol methods is described. The nanosized material was coated with carbon and
conducting polymers using several synthetic routes and precursors. A new synthetic route for the formation of nanoscopic LiFePO₄-PEDOT composite was developed. The composite was applied to an electrode in an optimised manner to maximise its use for high power applications.

The second chapter deals with a unique and original way of using templates to synthesise aligned, free-standing and ordered Fe₂O₃ micropillars. The growth of nanowhiskers of Fe₂O₃ on these micropillars was observed and studied. The Fe₂O₃ structures and their coated variants were further tested to be used as an anodic material in a Li-ion battery setup. Due to the highly specific dimensionality of the Fe₂O₃ micropillars, morphologic changes in the material during electrochemical cycling were observed much more noticeably. Additionally, the importance of a proper coating technique was substantiated.

Finally, the third chapter deals with synthesis of nanocrystalline vanadium nitride (VN), which was further tested as an anodic material. It was found that VN could reversibly intercalate one lithium per vanadium atom without any structural change and the carbon coated VN powder cycled stably at its theoretical capacity. This is the first time a binary nitride was shown to react reversibly with lithium without its structural decomposition. This leads us to tap on the superior stability of binary nitrides which could very well be the replacement for graphite in upcoming Li-ion batteries.

During the course of this work various synthetic methods such as hydrothermal, solvothermal and other solution based synthesis, solid state synthesis, synthesis by arc-welding techniques, flame pyrolysis etc. were used and electrode preparation as well as electrochemical cell setup were performed. The materials were analysed by techniques such as X-ray diffraction measurements, TEM and SEM investigations, magnetic and
conductivity measurements etc. Additionally, standard electrochemical characterisation techniques such as cyclovoltammetry, chronopotentiometry, galvanostatic measurements, coulometric and potentiometric titrations etc. were routinely performed.
Zusammenfassung

Die exponentiell wachsende Nachfrage nach “sauberen” Materialien mit herausragenden Eigenschaften hat die Lithium-Batterie Technologie dazu gezwungen, die Grenzen seines Könnens zu sprengen. Der moderne Mensch ist mit aller Art von portablen wiederaufladbaren Geräten vertraut, von Microchips bis zum Auto. Manche Durchbrüche seitens der Technologie werden erforderlich sein, um die Erwartung der zukünftigen Anwender auf nachhaltige und verbreitete Weise zu gewährleisten.

Zur selben Zeit hat die Entwicklung der Nanotechnologien ihre im Bezug auf die Forschung unermüdliche Expansion im Laufe des letzten Jahrzehnten fortgesetzt. Das Streben, Materialen als Nanopartikel darzustellen, um ihre neue elektronische oder mechanische Eigenschaften zu studieren, hat bis heute nicht nachgelassen. Trotzdem sind die Auswirkungen dieses Nano-Booms auf die Alltagsprodukte noch bescheiden.


Alle Materialien, die während dieser Arbeit synthetisiert worden sind, können als Nanopartikel bezeichnet werden. Da diese potentielle Kandidaten für die nächste Generation von Lithium-Ionen Batterien sind, erbringen sie volle Leistung nur auf Nanometerskala.

Das erste Kapitel beschreibt die Synthese von nanoskopischen LiFePO₄ durch solvothermal- und polyolprozesse. Das nach verschiedenen synthetischen Wegen und aus
unterschiedlichen Edukten erhaltene Produkt wurde mit einem Kohlenstofffilm und leitfähigem Polymer beschichtet. Das Kompositmaterial wurde so auf die Elektrode aufgetragen, dass seine Hochleistungseigenschaften optimiert sind.


Im Laufe dieser Arbeit wurden verschiedene synthetische Methoden (hydrothermal, solvothermal und andere nasschemische Verfahren sowie Festkörpersynthese mit Lichtbogen, Flammenpyrolyse usw.), Elektrodenvorbereitung und elektrochemische Messtechnik erlernt. Die Materialien wurden mit SEM, TEM, XRD, magnetische Messungen und u.a. Messungen der elektronischen Leitfähigkeit charakterisiert,
zusätzlich zu den standart elektrochemischen Messungen wie Cyklovoltammetrie, chronopotentiometrie, galvanostatische und coulometrische Messungen und potentiometrische Titrationen.