

氏 名 MAMUN, S. M. MOSTAFA AL

学位（専攻分野） 博士(理学)

学位記番号 総研大甲第578号

学位授与の日付 平成14年3月22日

学位授与の要件 数物科学研究科 物質構造科学専攻

学位規則第4条第1項該当

学位論文題目 Study on Electrode Materials for Lithium-Ion Batteries
by Neutron Scattering and X-Ray Diffraction

論文審査委員 主査 教授 池田 進
教授 永嶺 謙忠
教授 古坂 道弘
教授 新井 正敏
教授 大隅 一政
助教授 神山 崇（高エネルギー加速器研究機構）

論文内容の要旨

Lithium-ion secondary (rechargeable) cell technology is in its infancy. Many improvements including new cathode, anode, and electrolyte materials have been developed since the commercialization of the first Li-ion battery system in 1991 by Sony Corporation. Current commercial lithium-ion cells offer good performance but at a premium price in comparison to conventional rechargeable systems. In order to make Li-ion batteries more competitive, there must be improvements in performance and cost reduction without compromising the safety issues. Accordingly, through innovative cell design and the proper selection of materials, safety and performance can be enhanced and cost lowered in order to broaden its application and acceptance in the commercial market.

Research on the intercalation of carbon materials dates back to the 1950's. Much research has concentrated on the study of graphite intercalation compounds (GIC) for a long time. On the other hand fundamental aspects of electrochemical lithium intercalation into carbon materials other than graphite have been made since the lithium ion battery was first commercialized. People have been facing the difficulties in correlating electrochemical performances and structure because of the many different types of structural parameters that must be characterized in a single material. Therefore, the first task is to understand the structure correctly in order to discuss the intercalation mechanism, then improvement of the carbon anode can be achieved by structural designing.

Three kinds of carbon have been used as anodes for commercial lithium-ion cells: graphite, soft carbon and hard carbon. Graphite is three a three-dimensional ordered crystal that can intercalate up to a maximum of one lithium atom per six carbon atoms (LiC_6) giving a maximum capacity of 372 mAh/g^{-1} . Soft carbon and hard carbon constructed with two-dimensional ordered graphene sheets which are randomly stacked have a 'turbostratic' structure. Many soft carbons show a maximum reversible capacity when heat treated around 1200°C of about 300mAh/g^{-1} . Lithium can be doped to some hard carbons up to over one lithium atom per six carbon atoms and some of them offer over 500mAh/g^{-1} of reversible capacity with a small irreversible capacity of about 60mAh/g^{-1} .

Hard carbons play a significant role in recent developments of rechargeable Li-ion batteries. In addition to high capacity they also provide a significant performance in the potential range from 0 to 0.1V (vs. Li/Li^+). The capacity below 0.1V looks like a plateau during charge and discharge and is very attractive for anodes of high energy-density batteries. The charge-discharge mechanism studied by ^7Li -nuclear magnetic resonance ($^7\text{Li-NMR}$) suggested two types of Li species during lithiation process; one type of Li is the same as those in graphitizable carbons, and the other is quite different. The former is thought to be in the inter-layer space between graphene layers, and the latter is Li clusters with metallic character, which causes a significant capacity below 0.1V. In 1997 Y. Nishi proposed nanopore structure in hard carbons and these pores reversibly intercalate lithium which is the origin of high capacity. To rationalize the high "extra" lithium capacity of hard carbons, still a variety of

controversial models and explanations have been suggested in the literature. Yazami *et al.* (1995) proposed the formation of lithium multilayers on the graphene sheets. Peled *et al.* (1996) believe that the extra charge is attributed to the accommodation of lithium in “zigzag” and “armchair” faces between two adjacent crystallites and in the vicinity of the defects and impurities. Sato *et al.* (1995) suggested that lithium occupies nearest neighbour sites in intercalated carbons.

Neutron scattering technique is efficient to understand the structure of nongraphitizable carbons before and after Li intercalation. In the present study, the structures of the hard carbon and lithiated hard carbon were studied by small angle neutron scattering (SANS) to understand the structural changes during the lithiation process. In addition, Swedish natural graphite meso carbon microbeads (MCMB) were also studied as candidates for graphite and soft carbon by SANS and neutron powder diffraction (NPD). In-situ X-ray diffraction (IXRD) experiment was carried on jet-milled Swedish graphite to see if there is any influence of jet-milling on staging behaviour. From our study we can conclude the followings:

1. Small angle neutron scattering (SANS) measurement provided direct observation of nanopores and disordered structure in hard carbon. Lithium can be stored reversibly inside the pores by electrochemical intercalation resulting in higher reversible capacity (≈ 430 mAh/g) which is substantially greater than the maximum theoretical capacity (372 mAh/g) of graphite at LiC_6 composition.
2. During shallow lithiation process lithium first intercalates between the graphene layers of hard carbon which is concluded from the increase in d -spacing between the graphene layers, but no remarkable change in pore size was observed. Upon further deep charging d -spacing does not increase, but pore size increases indicating lithium intercalation into the pores.
3. Volume fraction of pores in hard carbon sample was measured $\approx 16\%$. We are much confident on this result because SANS technique is capable of probing every pore (open or closed, small or big) which is impossible by traditional gas adsorption techniques.
4. At low temperature (96 K) we did not observe any change concerning d -spacing and pore size in fully lithiated hard carbon.
5. Unlike hard carbon we observed that MCMB and Swedish natural graphite (Woxna Fines) do not contain any pore structure. They offer reversible capacity (305 mAh/g for MCMB and from 340 to 371 mAh/g between crude and jet-milled Swedish natural graphite) compared to hard carbon.
6. Jet-milling of Woxna Fines did not introduce any pore structure. However, from neutron powder diffraction (NPD) experiment we observed that the rhombohedral (ABC) phase content increased at the expense of hexagonal (AB) phase after jet-milling. This change in phase content increased the reversible capacity from 340 to 371 mAh/g.

論文の審査結果の要旨

Mamun 氏は、Li イオン電池に用いられるさまざまな炭素負極材料について中性子小角散乱の測定、粉末中性子回折実験、及び X 線回折実験を行い、そのナノスコピックな構造を初めて決定した。その結果、電池の充電にともない Li 原子が負極材料のどのような環境に入るのかを、構造解析の立場から直接的に明らかにすることに成功した。今後の電池のカーボン負極材料の開発の指針を与えることができると期待される。

世界中で、より性能の高い、充電可能な電池の熾烈な開発競争が行なわれてきている。すなわち、容量が大きく、充放電にともなう履歴が少なく、繰り返し充電に対して耐性のある電池が要求されている。そのようなものの一つとして Li イオン電池が実用化されており、現在は負極として炭素電極が用いられている。その炭素材料としては層状の結晶構造を持ったグラファイト、その構造が多少乱れたソフトカーボン、さらにその乱れが強いハードカーボンなどが使われている。このような電池を改良するにあたって、これまでは電気化学的方法による充放電特性の測定から炭素電極の特性を推測するしかなかった。Li 原子の炭素電極内での環境を推測するために NMR 測定が利用されることもあったが、炭素材料の構造に関する直接的データはまったく無い状態であった。

Mamun 氏は、高エネルギー加速器研究機構に設置されている、ナノスコピックスケールで非常に広い空間スケールに渡る測定が可能な中性子小角・広角散乱装置を用い、典型的な幾つかの炭素材料について中性子散乱実験を行った。その測定から、ハードカーボンの試料だけに特有の肩のある小角散乱を見つけた。これをモデル関数でフィッティングし、さらに散乱の絶対値を求めることにより、それがナノスケールのポイドからの散乱であることを明らかにした。また、そのポイドの大きさ、数、ポイドの全体に占める割合等を定量的に求めることが出来た。つまり、三種類の炭素材料のうち、ハードカーボンにのみナノスケールのポイドが多数存在することを明らかにし、そのポイドに Li が入ることで電池の容量が増えることを明らかにした。

また、これまでは充電に伴い Li が炭素のどのような環境に入るのかについては NMR による間接的な情報しか得られていなかったのに対し、中性子回折データで観測されたグラファイト構造の 002 反射の解析から、最初は充電に伴い層間距離が伸びること、さらに充電が進んでも層間距離は変わらないことを明らかにした。また小角散乱の解析から、ナノスケールポイドの大きさは最初は変化せず、充電が進んだときに大きくなるという結論を導きだした。つまり、ナノスコピックな炭素電極の構造解析により、Li は充電初期にはグラファイト構造の層間に侵入するが、さらに充電が進行するとポイドに侵入するという直接的証拠を得ることに初めて成功した。

さらに、NMR の研究から室温と低温では Li の存在環境が変わるのではないかというモデル提案もあったが、実際に中性子小角散乱で温度変化を測定し、散乱関数は全く変化しないこと、つまり、Li の侵入場所は温度によって変化しないことも明らかにすることができた。