The electrochemical behavior of silicon and graphite anode materials with different cathodes for lithium ion cells

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New material compositions with new electrode designs have the serious potential to improve the energy per weight and volume at reduced cost for lithium ion batteries. Herein, the advantage and disadvantage of electrode materials for LIBs were investigated in both half and full cells. It was found high capacity materials like silicon anode and Li-rich cathode provide higher specific capacity in mAh/g. In full cell configuration Graphite/Li-rich cathode had 92mAh/g specific capacity after 100 cycles at C/2.

1. Introduction
Lithium ion batteries (LIBs) are the energy storage systems which have widely application. The main components of lithium ion batteries are electrolyte, which provides a transferring medium for charged structures such as ions; anode, that is oxidized during the electrochemical reaction, gives electrons to the external circuit; and cathode that is reduced during the electrochemical reaction and takes electrons from external circuit. LIBs which are suitable for the most of the energy storage applications, have been studied with many research groups notably.

In an experimental study, Kim et al. [1] used commercial graphite and high-Ni layered oxide (LiNi0.6Co0.2Mn0.2O2). They reached discharge capacity of 208.4 mAh/g after the first cycle while it is around 200 mAh/g after 100 cycles at 0.2C. In another study Farmakis et al. [2] used silicon anode with Nickel Cobalt Aluminum Oxide (NCA), Lithium Iron Phosphate (LFP) and Lithium Cobalt Oxide (LCO) cathode. They indicated that the selection of cathode plays an important role to the complete electrochemical system and thus the long-term integrity of the cell. They had the highest capacity with LCO cathode as 132mAh/g after 40 cycles at 0.1C. Jana and Singh [3] were also used silicon as anode after milling from 24 h to 7 days. They used Lithium Nickel Cobalt capacity of ~76 mAh/g after 100th cycles. In this study, we used silicon and graphite anodes with Li-rich and NCA cathode to show the advantage and disadvantage of these commercial and new technology materials. It was understood that new technology materials show higher capacity in mAh/g after 100 cycles but still needed to increase the cycling stability.

2. Experimental study
2.1. Materials
Si was obtained from Nanostructured & Amorphous Materials, Inc. Graphite was purchased from TOB Machine and Celgard 2400 separator is obtained from Celgard. Poly (acrylic acid) (PAA) (Mw: 450,000, Sigma Aldrich) was utilized as binder. Electrolyte was purchased from BASF, including 1.2 M lithium hexafluorophosphate (LiPF6) in ethylene carbonate (EC), diethyl carbonate (DEC) (EC/DEC = 3:7 by weight), and 30% by weight of fluoroethylene carbonate (FEC) were added. NCA was purchased from NEI Corp. and Li-rich cathode was synthesized in Enwair Company. The composition of cathode active material was Li1.20Mn0.54Ni0.123-Co0.123-Al0.02O2. The same synthesis procedure was used with Ref. [4].

Silicon, binder and carbon black (CB) were mixed in water (weight ratio of Si nanoparticle/(PAA):CB: 70/20/10) for 3 h. Graphite anode was prepared in the ratio of 80/10/10 of active material/PVDF/CB and mixed for 3 h. The ratios were used as considering the previous experiences which can provide the higher active material content while keeping the suitable viscosity, conductivity and binding conditions. Slurries were coated on the copper foil by using a doctor blade. After electrodes dried, anode was calendared as 15% of the electrode thickness in roll press at 70 °C. The electrodes were cut as disk. They were placed in the glovebox...
overnight and further dried in the vacuum oven at 90 °C for 12 h. Fig. S1 (pictures from 1 to 5) shows the material and electrode preparation.

2.2. Cell preparation and testing

The performance of the assembled 2032 coin cells was evaluated with Neware Battery Test system. The cut-off voltage of anode half-cells are between 1.2 V and 0.01 V, assuming a theoretical value of 3500 mAh/g for Si and 372 mAh/g for graphite. For the cathode half-cell, the voltage was applied between 3.0 and 4.0 V for NCA and 3.0–4.55 V for Li-rich cathode assuming a theoretical value of 180 and 200 mAh/g, respectively. Half cells were cycled at C/25 for 2 cycles, at C/10 for 2 cycles and at 1C for 100 cycles. Full cells were cycled at C/2 for long cycling. Cyclic Voltammetry (CV) was conducted at 1 mV/s for each electrode. Anodes were tested between 0.01 and 1.2 V, while NCA and Li-rich cathode was tested 2.0–4.5 V and 2.0–5.0 V, respectively. The Fig. S1 (picture 6 and 7) shows the assembled coin cell and testing measurement.

3. Results and discussion

In Fig. 1a spherical silicon nano particles have the diameter between 50 and 65 nm which is consistent with the particle size distribution that shows the average particle diameter as 59 nm (0.059 μm) in Fig. 1c. The particle size of the cathode active materials directly affect the electrochemical performances of LIBs. According to SEM in Fig. 1b and 1d, Li-rich cathode material has the particle size in the range of 0.2–0.4 μm [5] while particle size analysis gives the average particle size as 6 μm. This difference can be explained with the agglomeration of nanoparticles in solution during the measurement.

Fig. 2 shows the result of half cells for each electrode and the result of full cells for the anode/cathode combinations. At the anode side, the capacity of silicon and graphite vs. lithium was compared. After 100 cycles, silicon showed ~1500 mAh/g capacity when graphite exhibited the specific capacity of 204 mAh/g. Although they were cycled at 1C, silicon showed excellent specific capacity. This is the result of high lithium storage property of silicon at room temperature (Li15Si4) [6] and on the other hand silicon can provide high capacities at nano-scale [7]. At the cathode side, the cells were exhibited 131 and 63 mAh/g specific capacity with Li-rich and NCA cathode, respectively after 100 cycles. The higher capacity of Li-rich cathode is provided by excess lithium in two phases: layered lithium manganate (Li2MnO3) and a layered lithium metal dioxide (LiMO2) structural unit. Li is first extracted from the layered LiMO2 structure up to a voltage of ~4.4 V in the first charge, and then the Li2MnO3 phase is activated with the extraction of Li2O as Li+, O2 and electrons from it at between 4.6 and 4.9 V [8]. This high discharge capability enables to reach the higher capacities.

The full cell with Graphite/NCA showed capacity failure when Graphite/Li-rich cathode had 92mAh/g after 100 cycles at C/2. The full cell with silicon anode was failed with both cathode electrodes. These data indicated that even silicon has a few times higher capacity than graphite anode according to half-cell result,
if cathode has the limited capacity, the cells fail. Even in other studies [9,10] NCA showed higher capacities, this can be explained that the synthesis conditions (metal salt type, methods, synthesis temperature etc.) [5,11] of material and test procedures can affect the cell performance. But in this study, all the electrodes were assembled in the same conditions and tested with the same procedure. Table S1 shows the electrochemical data comparison of recent studies on LIBs.

Fig. 2. Cycling graphs of Silicon and graphite anode materials with NCA and Li-rich cathodes.

Fig. 3. CV of silicon (a), graphite (b), and Li-rich cathode (c), NCA (d).
In CV, graphite and silicon showed completely different behaviour. In Fig. 3, at the first cycle there is a main anodic peak at around 0.6 V corresponding to the crystalline silicon. Upon cycles, the cathodic peaks are at 0.02 and 0.17 V to the lithiation reaction of Si to form Li2Si alloy, while the two anodic peaks are at 0.37 and 0.55 V. During the following cycles, the same peaks are observed. In the graphite case, after 1st cycle, there are obvious anodic peaks corresponding to delithiation process at around 0.44–0.47 V but there is no visible cathodic peak [12]. This results are consistent with the half cycling performance of the silicon and graphite anode that silicon showed good performance while graphite has lower capacity than its practical capacity [13].

When the NCA and Li-rich cathode were compared, it is seen that oxidation peak in the first scan of NCA occurs at a 4.05 V while the reduction peak occurs at 3.65 V. The anodic/cathodic peaks after 4 cycles at 3.69/3.92 and 3.95/4.26 V are ascribed to the oxidation/reduction process of Ni3+/Ni4+[14]. Cyclic voltammetry of Li-rich cathode showed the characteristic CV curves of the $\chi Li_2MnO_3(1-\chi)LiMO_2$ (M:metal) type materials, which had oxidation peak around 4.6 V [15]. The one at ~4.3 V corresponds to the oxidation of Ni$^{2+}/Ni^{4+}$ and Co$^{3+}/Co^{4+}$ in the layered phase. The corresponding cathodic peaks of Ni$^{4+}/Ni^{3+}$ and Co$^{4+}/Co^{3+}$ are observed at ~4.35 V and ~3.70 V, respectively. The cathodic peaks at ~3.25 V are attributed to Mn$^{3+}/Mn^{4+}$ [5].

4. Conclusion

Silicon and graphite anode were assembled with NCA and Li-rich cathode as full cell. Material characterization of high capacity anode and cathode showed that particles sizes of materials pretty good for cycling performance. According to cycle performances, silicon and Li-rich cathode showed excellent result in half cells while graphite and NCA had poor cycling performances. In full cells, the cells with silicon had drastic capacity fade while graphite/Li-rich combination exhibited promising results. CV of electrodes confirmed that each sample showed the characteristic peaks. This study can be a reference research for the cells for modified materials.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2020.127889.

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