Hard Carbon and Li$_4$Ti$_5$O$_{12}$-Based Physically Mixed Anodes for Superior Li-Battery Performance with Significantly Reduced Li Content: A Case of Synergistic Materials Cooperation

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ABSTRACT: Li$_4$Ti$_5$O$_{12}$ (LTO) and hard carbon (HC) are commonly used anodes in the Li-ion batteries. LTO has an operating voltage of 1.55 V and exhibits high-rate performance but with limited capacity. HC has high specific capacity but extremely low operating voltage. Herein, we show that a simple physical mixture of the two enhances the half-cell as well as full-cell performance through a synergistic cooperation between the materials. Specifically, the LTO–HC mixed anodes exhibit impressive performance even at high C-rates. This results from a quick internalization of Li ions by LTO followed by their distribution to HC regions via the high density of the winding internal interfaces between the two. The full cells of the LTO–HC mixed anodes with LiCoO$_2$ (LCO) evince an enhanced operating voltage window and a well-defined plateau. Because of a reduced irreversible capacity loss in the LCO/mixed anode full cells, the overall specific capacity is better than the LCO/pristine anode full cells. Also, with the LTO–HC 20–80 anode (Li content reduced by 80%), the full cell exhibits an impressive performance when compared to pristine anodes without pre-lithiation. The LCO/mixed anode full cells have excellent cycling stability up to 500 cycles at a current density of 100 mA g$^{-1}$.

INTRODUCTION

Li-ion batteries are the suitable choice for most of the practical applications such as portable electronics and hybrid/electric vehicles because of their durability, high power and energy density, long cycle life, and low self-discharge rate. There have been numerous developments made on the electrode materials appropriate for the Li-ion batteries to achieve state-of-the-art performance from the device and mitigating the problems faced during implementation on the real systems. For any practical or commercial application, the battery must deliver fairly high power density as well as energy density with minimal capacity fade during cycling. To accomplish these requirements, various anode materials have been investigated, graphite being the most popular among all. An ideal anode material should have a low intercalation potential for Li insertion/de-insertion, short paths for ion diffusions leading to high rate capability, low volume expansion during lithiation and de-lithiation, low cost, and environmental-friendly character.

Among the various anodes investigated so far for the Li-ion batteries, Li$_4$Ti$_5$O$_{12}$ (LTO) is well-known owing to their superior characteristics. LTO exhibits a well-defined operating voltage of 1.55 V and a specific capacity of 175 mAh g$^{-1}$, making it useful for practical applications. It has high rate capability, good cycle life and, importantly, a negligible volume expansion during charging and discharging. LTO has the spinel structure and it transforms into a rock salt structure (Li$_4$Ti$_5$O$_{12}$) during discharging, which has lattice parameters comparable to the spinel structure. The process takes place by the migration of Li ions from the tetrahedral sites to the octahedral sites and the three incoming Li ions occupying the vacant tetrahedral sites and moving to octahedral sites. The overall reaction mechanism is given in the equation below

$$3\text{Li} + \text{Li}_4\text{Ti}_5\text{O}_{12} \leftrightarrow \text{Li}_7\text{Ti}_5\text{O}_{12}$$

The structural transformation is reversible and is called topotactic as the final structure is similar to the parent one. However, in spite of all these features, LTO has not been considered as the optimum choice as an anode material for practical devices because of some of its intrinsic limitations. Specifically, LTO has poor electronic conductivity and owing to its low specific capacity, it is considered as a low energy density anode material. To overcome these issues, various interesting strategies have been developed such as making LTO composites with conducting materials such as carbon or metal nanoparticles, making nanostructured LTO, or coating LTO with hard or soft carbon by ball milling, chemical vapor deposition, or pyrolysis methods. However, these
methods are expensive and elevate the overall cost of the battery including the complexity in synthesis.

Hard carbon (HC), on the other hand, is another good choice for the Li-ion battery anode because of its high reversible capacity and lower Li intake potential.\textsuperscript{17} HCs are commonly derived from biomass by a simple pyrolysis treatment, thus representing a cheap material for battery application.\textsuperscript{18} HC, being non-graphitizable, has its planes randomly oriented with enhanced d-spacing.\textsuperscript{19} Though it has a low surface area, it is still considered to be a high energy density material as it has high specific capacity. As proposed by Stevens and Dahn,\textsuperscript{20} HC stores ions by intercalation as well as adsorption. The intercalation occurs in the graphitic planes of the carbon in the voltage range of 1–0.1 V represented by the sloping region in the discharge curve.\textsuperscript{21} The sloping nature of the curve indicates that the voltage varies for every Li site available. The adsorption occurs at very low voltages lying close to metal plating in the micro- or nanopores of the carbon where a large number of ions get trapped and can be extracted only at extremely low current densities.\textsuperscript{22} These ions are irreversibly trapped, causing a huge first cycle capacity loss.\textsuperscript{23} This limits the rate performance of the material and thereby the power density, making it inappropriate for potential use. To address this problem, HCs are functionalized with dopants or nanoparticles to enhance the specific capacity and operating window.\textsuperscript{24,25}

In this work, we propose and demonstrate that a simple physical mixture of LTO and HC as an anode has several advantages in terms of enhanced performance factors through synergistic effects. Interestingly, because of the specific scientific reasons outlined in the course of the discussion, this simple approach combines the advantages of the individual anodes and diminishes their respective shortcomings, eliminating the need to use any complex synthesis protocol. We have investigated such LTO–HC mixed anodes in half-cells at various C-rates as well as at fairly high fixed values of constant current densities. Moreover, the full cells have also been tested with LiCoO\textsubscript{2} (LCO) to prove that the Li content of anodes can be dramatically reduced to as low as 20%, still retaining the high-performance factors without any pre-lithiation process involved. Thus, this work proposes a facile methodology to gain high power as well as energy density of a full-cell device without the use of any tedious procedure, thereby reducing the cost and processing complexity or time.

\section*{RESULTS AND DISCUSSION}

The powder X-ray diffraction (PXRD) data for LTO and HC are given in Figure S1. The XRD pattern for LTO (Figure S1a) can be indexed to the cubic spinel structure with the space group Fd\textsubscript{3}m according to the literature (JCPDS file no. 49-0207). The XRD for HC (Figure S1b) consists of the broad peaks representing (002) and (100) planes of amorphous carbon at the 2\theta values of 23.6° and 43.8°, respectively.\textsuperscript{12}

**Electrochemical Data. Impedance Spectroscopy.** Figure 1a illustrates the impedance spectra of all the four samples before cycling. The higher frequency regions of the Nyquist plot consist of a semicircle which is the measure of the charge transfer resistance at the electrode surface.\textsuperscript{26} The series resistance is found to be less in all the samples. The charge transfer resistance of the pristine LTO electrode is the lowest among all cases in this case. The Nyquist plot for HC exhibits a larger semicircle at high frequency owing to the higher charge
transfer resistance at the electrode surface. At low frequencies, the Warburg component, that is, the sloping line corresponds to the diffusion process occurring in the bulk material. The LTO–HC 20–80 mixed anode impedance resembles that of pristine HC, whereas that of the LTO–HC 50–50 mixed anode exhibits a second semicircle. The semicircle at high frequencies corresponds to the diffusion through pores of the electrode. The mid-frequency semicircle represents the charge transfer resistance and the constant phase element (CPE) at the electrode–electrolyte interphase. The occurrence of these two could also be attributed to the non-homogenous electrode composed of small and big particle sizes as discussed at length by Xu et al. In the plot, the LTO anode shows slow diffusion. As for the present case of mixed material anodes, such type of the Nyquist plot has indeed been observed in electrodes containing components having different particle sizes, big and small, and they have been studied and discussed extensively earlier. The slow diffusion in such cases has been attributed to the non-homogeneity of the electrode surface, the thickness, and the difference in particle sizes of the materials. When two differently sized particles are present and the calendaring of the electrode is not uniform, then the surface inhomogeneity leads to the development of an arc in the middle-to-low-frequency region and results in the inclination of impedance curve toward the real impedance axis. As LTO and HC have different particle sizes, the electrode surface will be inhomogeneous, causing unequal distribution of mass that leads to a shift in the semicircle near the low frequency regions. After 5 cycles, all electrodes exhibit a semicircle with a reduced charge transfer resistance in the high-frequency region and the low frequency region corresponding to bulk ion diffusion, as shown in Figure 1b. The 50–50 case and the pristine LTO are similar, whereas the 20–80 case is close to the pristine HC in nature.

Cyclic Voltammetry. The CV curves of the samples are presented in Figure 1c,d. The pristine LTO cathodic scan has an intercalation peak at 1.5 V and a small peak at 0.7 V. During the anodic scan, the de-intercalation peak occurs at 1.6 V. The redox peaks are consistent in the subsequent cycles. The first cycle CV for HC consists of three broad peaks along with the intercalation peak below 0.1 V in the reverse scan. The peak at 0.65 V is due to the solid electrolyte interface (SEI) formation and disappears in the next cycle. The redox peaks at 0.93 and 1.03 V are also present in the first cycle and can be seen in subsequent cycles with a small shift. The peak at 0.19 V could be attributed to side reaction or irreversible ion adsorption and is absent in later cycles. The CV of the mixed anodes reveals the characteristic peaks of both LTO and HC as evident from the CV curve of LTO–HC 50–50 and LTO–HC 20–80.

Galvanostatic Charge–Discharge. The half-cells were first discharged at a low current density of 50 mA g⁻¹ to facilitate uniform SEI layer growth on the electrode surface. The nature of the charge–discharge curves shown in Figure 2 explains the dual character of the mixed anodes when compared to the pristine ones. The LTO anode has a plateau at a high voltage of 1.55 V, whereas HC has a sloping nature at a high voltage but a plateau near to 0.01 V. The LTO–HC 50–50 discharge curve has a flat plateau at a high voltage corresponding to the Li insertion potential of LTO as well as the sloping region from 1 to 0.1 V corresponding to the HC intercalation potential in the equal proportion. The LTO–HC 20–80 mixed anode partially exhibits the LTO character, with the HC character dominating the charge–discharge profile. The mixed anodes give high capacity as compared to the pristine anodes because of the enhanced electrochemical window from 1.55 to 0.01 V, whereas this advantage is not there in the case of individual anode materials (in LTO, it is 1.55 V and in HC, it is 0.1–0.01 V approx.). The theoretical capacities of LTO and HC are 175 and 372 mA h g⁻¹, respectively. The calculated capacities for the mixed anodes considering the weight ratio are 273 mA h g⁻¹ for LTO–HC 50–50 and 332.6 mA h g⁻¹ for LTO–HC 20–80. As seen from the curves, the realized capacity of HC is much lower than the predicted value which implies that the ion adsorption sites in HC are not accessible to Li ions to the full extent and need very low current densities to be filled (adsorption in nanopores of HC). The reason for the excess capacity in the mixed anode cases is the quick internalization of ions facilitated by LTO and then the distribution of ions in the HC channels or the nanopores. The process of quick Li-ion internalization afforded by LTO thus helps these ions access more sites of HC at the same current density, hence the higher capacity reflected at that current density. This way, the capacity close to the predicted value is achieved in the mixed anodes as proven by our charge–discharge measurements, which is not the case with pristine HC because of its poor rate capability at the same current density. The rate performance of the samples was checked at different C-rates given in the Supporting Information. Figure S2 elucidates the rate performance of all the samples along with the Coulombic efficiency. The cells were cycled at high rates of 20 C. As is evident, pristine LTO, being the high rate capability anode, does not undergo much degradation in the specific capacity even at 20 C and gives a
specific capacity value of about 145 mA h g$^{-1}$, whereas for the HC case, the specific capacity drops down drastically when subjected to high C-rates and the specific capacity falls down to 90 mA h g$^{-1}$. Interestingly, the LTO–HC mixed anodes perform superior to individual anodes at high rates, and the specific capacity lies close to that of pristine LTO. Thus, the LTO–HC 50–50 mixture anode exhibits a specific capacity of 130 mA h g$^{-1}$ at 20 C, whereas the LTO–HC 20–80 mixture anode gives a capacity of about 145 mA h g$^{-1}$. The electrodes were also cycled at constant current densities evinced in Figure 3. At high current densities of 2 and 6 A g$^{-1}$, the mixed anodes possess an extremely impressive performance and high cycling stability up to 3000 cycles with minimal capacity fade. In these cases as well, HC fails to withstand high current densities, whereas the mixed LTO–HC electrodes function almost similar to LTO in spite of a very significant reduction in the Li content in the anode. The possible reasons for this interesting outcome have been discussed below in the Mechanism of Charge Storage section.

**Mechanism of Charge Storage.** Scheme 1 illustrates the proposed mechanism of the Li-ion storage in the case of the mixed anodes as compared to the pristine material anodes. As is well-known, LTO has well-defined Li insertion sites and because of small diffusion paths for ion migration from 8a tetrahedral sites to 16c octahedral sites of the spinel structure,

Figure 3. Cycling stability at constant current densities. (a) At 2 and (b) at 6 A g$^{-1}$.

Figure 4. SEM images of electrodes. First row: bare electrode; second row: after first discharge; third row: after 10 cycles; and fourth row: after 200 cycles.
the rate capability is high, but the capacity is low because of the limited Li-ion vacancies as explained in the introduction above. Because of high-rate capability, the LTO capacity does not drop when the current density is raised from a low to a high value. On the other hand, HC has turbostratic planes and no direct channels or sites for ions as in the LTO case. Moreover, HC consists of nanopores and thus, to realize its full capacity, it has to be charged at very low current densities for all pores to get filled. Thus, the HC anode gives high capacity at low current densities, but very low capacity at high current densities as the Li ions are not able to access all the available sites. As seen in the mixed anode cases, the capacity is enhanced and the rate performance is also improved because of the channelized distribution of the ions. The presence of LTO facilitates quick Li uptake even at high rates, and HC provides additional sites for their localization on the surface of the electrode. The synergistic effect of quick internalization of Li ions by LTO and its re-distribution to the HC across the internal effective large area winding interfaces between LTO and HC provides high power as well as energy density in the mixed materials anode case. This is true for the case where Li content is reduced even up to 80%

**Full Cells with LiCoO₂.** For full-cell fabrication, the LCO cathode was used. The half-cell performance of LCO is given in

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**Figure 5.** Full-cell performance with LCO of (a) LTO; (b) HC; (c) LTO–HC 50–50, and (d) LTO–HC 20–80 anodes. (e) Cycling stability at 100 mA g⁻¹ of all full cells.
the Supporting Information in Figure S3. LCO gives a specific capacity of 165 mA h g⁻¹ at 50 mA g⁻¹.

The full cells were tested at C/4 rates, and the curves are presented in Figure S4. The LCO/LTO full cell gives a specific capacity of 85 mA h g⁻¹ with a negligible irreversible capacity loss. The full-cell operating voltage is from 1.8 to 2.5 V and has a plateau at 2.35 V. It was found that if the full cell is charged beyond 2.5 V, there is a rapid decay in the specific capacity, and the cell is not stable in that voltage window. The LCO/HC full cell has the first charging capacity of 130 mA h g⁻¹ but has a substantial capacity loss of about 60 mA h g⁻¹, giving an overall cell capacity close to 70 mA h g⁻¹.

The LCO/LTO—HC 50–50 full cell also undergoes an irreversible capacity loss of 20 mA h g⁻¹ but still gives an impressive specific capacity of 100 mA h g⁻¹, which is higher than that of the LTO and HC-only full cells with LCO. The LCO/LTO—HC 20–80 full cell (with dramatic reduction of Li content in the anode) also performs better than the individual anode half-cells but has an irreversible capacity loss of 40 mA h g⁻¹, giving a full-cell reversible capacity close to 95 mA h g⁻¹. The important achievement in these two cases is the enhancement of the operating voltage window of the full cells and the specific capacity leading to enhanced power and energy density of the full-cell device without any pretreatment of the anode such as pre-lithiation. Also, the nature of the full-cell charge—discharge depends on the anode characteristic. The LCO/LTO full cell has a plateau at 2.35 V, whereas the LCO/HC full cell has a sloping curve with no constant operating potential, a limitation in the device application. When the mixed LTO—HC 50–50 and 20–80 materials are used against LCO, a plateau region at 2.35 V is seen with an enhanced potential window up to 3.5 V, giving higher specific capacity.

The full cells were also tested at a high current density of 100 mA g⁻¹ for cycling stability, and the charge—discharge curves are specified in Figure 5. The LCO/LTO full cell has a specific capacity of 50 mA h g⁻¹ and is stable up to 250 cycles but subsequently starts degrading. The LCO/HC full cell gives a reversible capacity of only 30 mA h g⁻¹ and suffers from constant capacity fade. The LTO—HC 50–50 and LCO-based full cell has the highest specific capacity of 55 mA h g⁻¹ and is highly stable up to 500 cycles without any capacity fading. The LCO/LTO—HC 20–80 full cell has a slightly lower value as compared to LCO/LTO and LCO/LTO—HC 50–50 full cells (40 mA h g⁻¹) but is still much higher than the LCO/HC full cell with excellent stability up to 500 cycles. The corresponding energy densities of the full cells are 34 Wh/kg for LCO/LTO, 24 Wh/kg for LCO/HC, 35 Wh/kg for LCO/LTO—HC 50–50, and 40 Wh/kg for LCO/LTO—HC 20–80. We gain in terms of high energy density owing to an enhanced operating potential window. The LCO/HC full cell suffers from a substantial irreversible capacity loss and thus lacks stability as well as reversible capacity retention. Also, when subjected to a high current density of 100 mA g⁻¹, the LCO/pristine anode full cells do not perform well, whereas the LCO/LTO—HC mixed anodes are superior with the power density enhancement of the full cells.

CONCLUSIONS

Li-battery anodes are prepared by a simple physical mixing of two anode materials, namely LTO and HC, with different strengths and weaknesses in terms of capacity and rate capability properties, in different proportions. Interestingly, the performance of such mixed anodes is found to be superior to that of the individual material (LTO or HC) anodes, which can be attributed to a synergistic effect of rapid internalization and internal re-distribution of Li ions. This condition also represents a rather unique case of a laterally inhomogeneous SEI which is highly stable, possibly because of its ability for stress accommodation. In the full cells with LCO cathodes, the LTO—HC mixed anodes flaut much higher stability than only LTO- or HC anode-based full cells. Importantly, the Li content in the anode can be reduced by as much as 80%, and no pretreatment is performed on the anodes to achieve a desirable level of performance. At a high current density of 100 mA g⁻¹, the LTO—HC mixed anodes full-cell performance is excellent, and the operating voltage window is also enhanced for full-cell operation.

EXPERIMENTAL SECTION

Materials and Methods. LTO and LCO procured from Sigma-Aldrich and commercially available HC were used as received. The mixed anodes were prepared by taking LTO and HC in two proportions: 50–50 and 20–80 by weight. The slurry was made by mixing the anode powders with Super P and polyvinylene fluoride binder in the ratio of 80:10:10 and N-methyl-2-pyrrolidone as the solvent. The slurry was coated on the Cu foil and was kept for drying overnight at 80 °C. The slurry was coated on the Cu foil and was kept for drying overnight at 80 °C. The foil was then punched into 1 cm² circular discs. PXRD was done using a Bruker D8-ADVANCE X-ray diffractometer (Germany) with Cu Kα (wavelength = 1.5418 Å). SEM was done using an FEI Nova Nano 450 SEM instrument.

Electrochemical Measurements. The 2032 coin cells were made using mixed anodes, Li metal, and Whatman separator known as half-cell configuration. The full cells were fabricated using LTO and HC mixed anodes and the LCO cathode. The electrolyte used was commercial LiPF₆ in ethylene carbonate and dimethyl carbonate (in the volume ratio of 1:1). Galvanostatic charge—discharge measurements were done with BTS-Neware (China) 5 V, 10 mA battery tester. The impedance and cyclic voltammery were done with a VMP3 biologic system equipped with potentiostat and galvanostat channels. The mass loading of the electrodes is in the range of 1.3–1.5 mg. The cathode to anode mass ratio is 1:1 for LTO and 1.5:1 for LTO—HC 50–50, LTO—HC 20–80, and HC. The electrolyte was the same for full cells. The full-cell fabrication was done using 2032 coin cells with a Whatman separator. The full-cell measurements were done considering the weight of both the cathode and the anode in all the cases.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01659.

PXRD of LTO and HC, rate performance of all samples, LCO charge—discharge curves and rate performance, charge—discharge curves of full cells at the C/4 rate, PXRD plots of samples after first discharge (PDF).

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