

Low voltage anode materials for lithium-ion batteries



Ali Eftekhari^{a,b,*}

^a The Engineering Research Institute, Ulster University, Newtownabbey BT37 0QB, United Kingdom

^b School of Chemistry and Chemical Engineering, Queen's University Belfast, Stranmillis Road, Belfast BT9 5AG, United Kingdom

ARTICLE INFO

Keywords:

Anode materials
Lithium-ion battery
High voltage battery
Low voltage anode
Pseudocapacitive anode materials
Supercapacitors

ABSTRACT

Studies of anode materials due to the rapidly growing demand for lithium-ion batteries (LIBs) are an active area of research. However, the primary focus is on the specific capacity and cyclability. An essential requirement of electrode materials is the operating voltage, which is defined by the redox potential, but there is a tendency to sacrifice this feature in favor of higher capacities. For the cathode materials, there is a common categorization based on the operating voltage (e.g., high voltage cathode delivering a redox potential between 4.5–5.0 V vs. Li/Li⁺), but there is no such categorization for anode materials. The present manuscript aims to provide a general review of the anode material to highlight the importance of the operating voltage for an anode candidate. Furthermore, it is described that compositing the anode materials with carbon nanomaterials can increase the specific capacity for the delithiation, but part of this capacity is due to the carbon capacitance or pseudocapacitance mostly occurring at high potentials, which cannot be gained in the full cell performance. This class of pseudocapacitive anode materials can be of potential interest for energy storage but not appropriate candidates for the conventional LIBs. It is also emphasized that the delithiation process is the main duty of an anode material when a LIB is working.

1. Introduction

The initial challenge of lithium-ion batteries (LIBs) was to find suitable cathode materials facilitating the Li intercalation/de-intercalation redox system at a relatively high potential (e.g., 4 V vs. Li/Li⁺). The first interesting feature of LIBs is the negative potential of the Li anode, which provides a rare opportunity to have a high cell voltage. On the other hand, the Li/Li⁺ redox system provides a stable and reliable electrochemistry, which is also employed as the reference electrode in the majority of works in the realm of LIBs. As a result, the conventional three-electrode electrochemical cells have been replaced by the two-electrode cells in studies of LIBs, in which the anode and reference electrode are a metallic Li electrode.

However, the safety risk of utilizing metallic Li has made it an impractical anode material. Hence, the quest for finding suitable anode materials was also an active area of research for advancing the LIBs. Two unbeatable features of Li anode are somewhat sacrificed when employing another anode material: the redox potential is more positive in comparison with Li/Li⁺, and the specific capacity is obviously lesser than that of metallic Li. The first choice to replace the metallic Li anode was graphite, which has been widely employed in the commercial LIBs. The theoretical capacity of graphite anode is 372 mA h g⁻¹, and its redox potential is slightly higher than that of the metallic Li anode. As a result, the operating voltage of the LIBs is shifted to 3 V level instead of

4 V. Having a slightly more positive potential than Li/Li⁺ for the anode has some advantages, as reaching the less positive potentials close to 0 vs. Li/Li⁺ may result in the formation of lithium dendrites and a blocking solid electrolyte interphase (SEI). A possible approach is to utilize high-voltage (the so-called 5-V) cathode materials to compensate the anode excess potential [1], though 5-V cathode materials are somehow unstable due to the presence of transition metals at their high oxidation valences [2].

Fig. 1 shows that even when an anode material with a well-defined flat plateau at 2.0 V vs. Li/Li⁺ coupled with a 5 V cathode, the cell voltage is just less than 3 V. This suggests that an anode material with a more positive potential is not practical. On the other hand, the absence of a flat plateau can turn the battery into a supercapacitor [3,4].

Since the theoretical capacity of graphite is almost achieved practically, there is a demanding interest in finding new anode alternatives. Therefore, the focus is on anode materials with high specific capacities. However, the importance of the anode negative potential is somehow neglected. This can be understood by the wide potential window, which is usually employed for the investigation of the anode materials. Owing to the rapidly growing demands for the electrochemical energy storage systems, there are always new possibilities for designing new types of storage devices. Thus, such high-voltage anode materials can find superior positions in new electrochemical systems. However, it is unlikely to consider an anode material

* Correspondence address: The Engineering Research Institute, Ulster University, Newtownabbey BT37 0QB, United Kingdom.

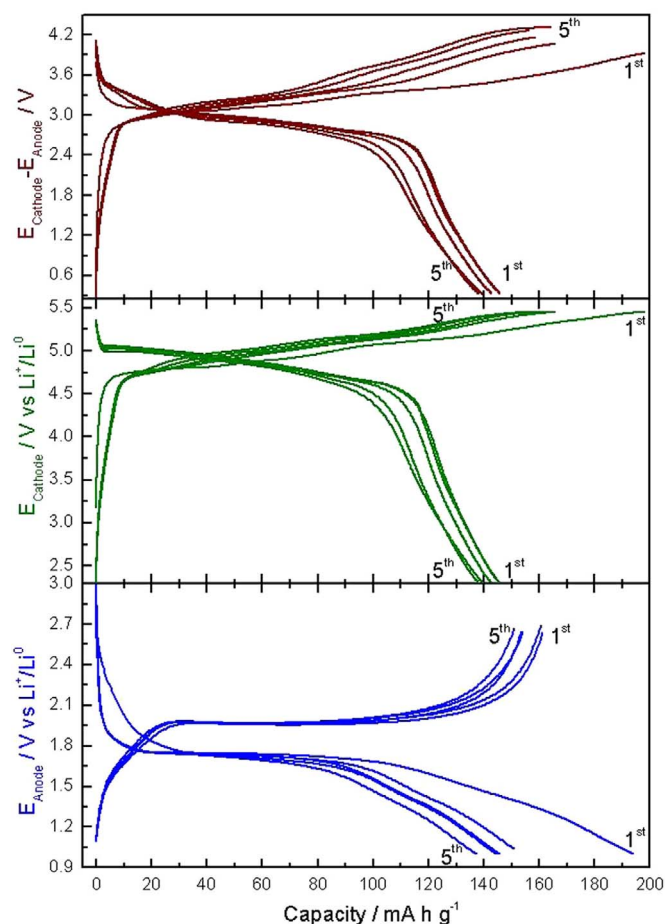


Fig. 1. Galvanostatic charge/discharge cycles representing the $E_{\text{cathode}}-E_{\text{anode}}$ vs. capacity of $\text{ntTiO}_2/\gamma\text{-Li}_3\text{PO}_4/\text{Li}_2\text{CoPO}_4\text{F}$ cell. This figure includes the voltage profiles of the cathode (E_{cathode} vs. capacity) and the anode (E_{anode} vs. capacity) in the middle and bottom plots. The capacity of the full cell is calculated using the cathode mass. Reproduced with permission from Ref. [1]. Copyright 2016, Nature Publishing Group.

with a redox potential higher than 2 V vs. Li/Li^+ as a promising candidate for the anode of current LIBs.

One may argue that reducing the operating voltage in favor of the energy density is a practical approach, as the overall voltage can be compensated by using the cells in series. However, when the operating voltage is below 2 V, the conventional LIB architecture loses its justification, as alternative aqueous batteries can be more economical and safer. The importance and requirement of delivering a sufficiently low potential for anode materials are somehow diminishing, as some authors do not even illustrate the galvanostatic profiles or voltammetric data and simply focus on the specific capacity without mentioning the operating voltage (see for example, [5]).

The present manuscript reviews the current anode materials from a different perspective to highlight the importance of the operating voltage as well as the specific capacity. Here, it is not aimed to provide a complete list of all anode materials with potentially low-voltage performance. Instead, we attempt to provide general examples from most common classes of the materials. This should clarify the overall concept.

2. Electrochemical studies of anode materials

The fundamental investigation of anode materials in a half-cell is sometimes misleading. Anode materials are normally investigated as a cathode in the standard two-electrode cell in which the metallic Li is employed as the anode and reference electrode. The first issue is connected with the direction of charging and discharging. In a full cell,

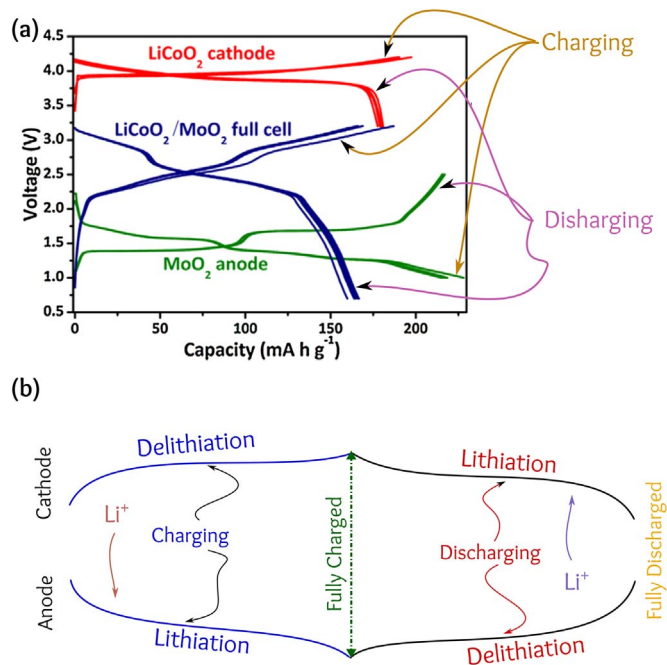


Fig. 2. (a) The electrochemical performance of $\text{MoO}_2\text{-LiCoO}_2$ full cell. The galvanostatic discharge-charge curves of LiCoO_2 cathode, $\text{LiCoO}_2\text{-MoO}_2$ full cell and MoO_2 anode at a current rate of 1 C for initial five cycles. (b) A schematic illustration of the performance of the half cells. Reproduced with permission from Ref. [234]. Copyright 2016, Elsevier.

charging process includes the lithiation of the anode and de-lithiation of the cathode (Fig. 2). As a result, the cell will reach its fully charged status in which the cell voltage is maximum (*i.e.*, most positive potential of the cathode and most negative potential of the anode). During the discharging process, the anode undergoes delithiation in which its potential increases to more positive values and the cathode undergoes the lithiation in which its potential decreases to less positive potentials. When the cell is fully discharged, the operating voltage reaches its minimum value (*i.e.*, least positive potential of the cathode and most positive potential for the anode). Therefore, charging and discharging of the anode and cathode undergo opposite directions. The importance of this labeling is when the charge and discharge capacities or potentials are significantly different.

In both anode and cathode cases, the capacity of interest is the reversible capacity for the lithiation/de-lithiation. This means that the capacity of an anode material is not x for the Li storage if we can intercalate $x\text{Li}$ but de-intercalate only $x/2$. This is the reason that the irreversible capacity reported during the first charge/discharge cycle is not reliable. Instead, the first cycle, at least in many cases, should be considered as a part of the electroactive material preparation. Fig. 3 shows typical galvanostatic profiles of a series of porous graphene electrodes. The high lithiation capacity is usually interpreted as the Li storage capacity, but it is not true. The real capacity of Li storage should be read from the delithiation profile, as the intercalated Li should be reversibly deintercalated; otherwise, it is useless. This is the case for some intercalation lithium metal oxides (including cathode materials) in which Li can be intercalated but cannot be fully deintercalated. However, this is not the case for pseudocapacitive materials such as porous graphene. The electric charge presented by the lithiation profile is not fully for the lithiation process but also an irreversible process such as Li electroplating at the reactive sites of the carbon or the reactions associated with the formation of SEI.

Comparing the first two cycles displays that the delithiation amount remains intact while the lithiation capacity is declining. If assuming that the electric charge recorded is due to the lithiation, the amount of Li intercalated during the lithiation is three times more than that deintercalated. Even during the second cycle, an excess Li is inter-

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