Batteries

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Critical Requirements for Rapid Charging of Rechargeable Al- and Li-Ion Batteries**

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Electrochemical energy storage devices for modern mobile electronics, electric vehicles, and even grid storage are expected to provide large gravimetric capacity within a limited space, while also having the lowest possible manufacturing costs. Lithium-ion batteries (LIBs) have been successful in terms of meeting the energy density requirement; however, the LIB manufacturing cost is still too high for these devices to be applied to large-scale battery systems. Compared with LIBs, multivalent-ion batteries such as Al- and Mg-ion devices can potentially offer both low cost and high energy density.[1] These elements are significantly heavier than lithium; however, this disadvantage is compensated for by their facility for multi-electron transfer during electrochemical ion insertion and extraction, which can provide additional gravimetric capacity. In this regard, multivalent-ion batteries have been identified as high-performance and inexpensive electricity storage devices for use in next-generation energy technology.

Meanwhile, considerable effort has been made by researchers to improve the power density of current battery technology to meet the demands of modern lifestyles.[2] However, it is difficult to expect high rate capability from a multivalent-ion system, because of the very strong electrostatic repulsion between the highly charged ion and the cations in the host materials. Thus, these systems may suffer from slow charge and discharge rates, owing to the high activation barrier for ion insertion and extraction and even for ion diffusion in the host structure. Ideally, the charging time should be minimized as much as possible. Therefore, obtaining a fast charge and discharge rate performance is considered a major challenge for both multivalent-ion battery systems and LIBs. Herein we briefly describe recent approaches to overcoming this problem.

The requirements for next-generation energy technology are well reflected in the recent paper by Dai and co-workers.[3] They use an Al/graphite cell composed of an Al-foil cathode and a graphite anode, separated by an ionic-liquid electrolyte of 1-ethyl-3-methylimidazolium chloride and anhydrous aluminum chloride. In this device, the metallic Al and dissolved $AlCl_4^-$ on the cathode side were converted into $Al_2Cl_7^-$ during discharging, and $AlCl_4^-$ was de-intercalated from the graphite layer at the same time (Figure 1 a). The reverse reaction occurred during charging. In that study, the cell exhibited a reversible capacity of approximately 65 $\mathrm{mAh\,g^{-1}}$, based on the cathode mass. This value can be compared to the first work on an Al/graphite cell, which was conducted by Gifford and Palmisano in 1988. They reported that the Al/graphite cell exhibited a reversible capacity of approximately 35 $\mathrm{mAh\,g^{-1}}$ using an ionic-liquid electrolyte consisting of 1.5:1 $AlCl_3$:1,2-dimethyl-3-propylimidazolium chloride.[4] They concluded that the graphite electrode could provide a reversible intercalation of chlorine (the Cl^- ion). On the other hand, Dai et al. revealed that the intercalation species in graphite consists of both Al and Cl, as confirmed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). In addition, they combusted the fully charged graphite electrode at 850 °C in air and obtained Al_2O_3, which was direct evidence of Al intercalation during the charging. Moreover, they found the Al/graphite cell had a lower Coulombic efficiency and cycling stability when electrolytes with higher water content were used. By lowering the water content in the cell, they successfully demonstrated a very stable cyclability of 200 cycles at 1 C (current density: 66 $\mathrm{mA\,g^{-1}}$) without capacity fading, and a significantly higher working voltage (ca. 2 V) than that of other reported rechargeable aluminum battery systems.[4,5]

The use of intercalation cathodes for multivalent-ion batteries faces a major challenge with regard to fast ion-insertion/-extraction into/from the host materials during charging and discharging, respectively. This is because a high multivalent ion charge concentration or a large complex-ion ionic radius leads to poor insertion and extraction kinetics. Dai et al. further investigated flexible graphitic foam as a cathode material and current collector (Figure 1 b). Remarkably, a cell based on three-dimensional (3D) graphitic foam had an innovative performance in terms of both rate capability and cyclability. No evidence for capacity fading was observed up to 7500 cycles at an ultrahigh current density of 4000 $\mathrm{mA\,g^{-1}}$ (Figure 1 d; 4000 $\mathrm{mA\,g^{-1}}$ corresponded to ca. 60 C and each cycle was only ca. 2 min in duration, 1 C $\approx$ 65 mAh). Moreover, the cell retained its capacity and cyclability over a range of charge and discharge rates (1000–

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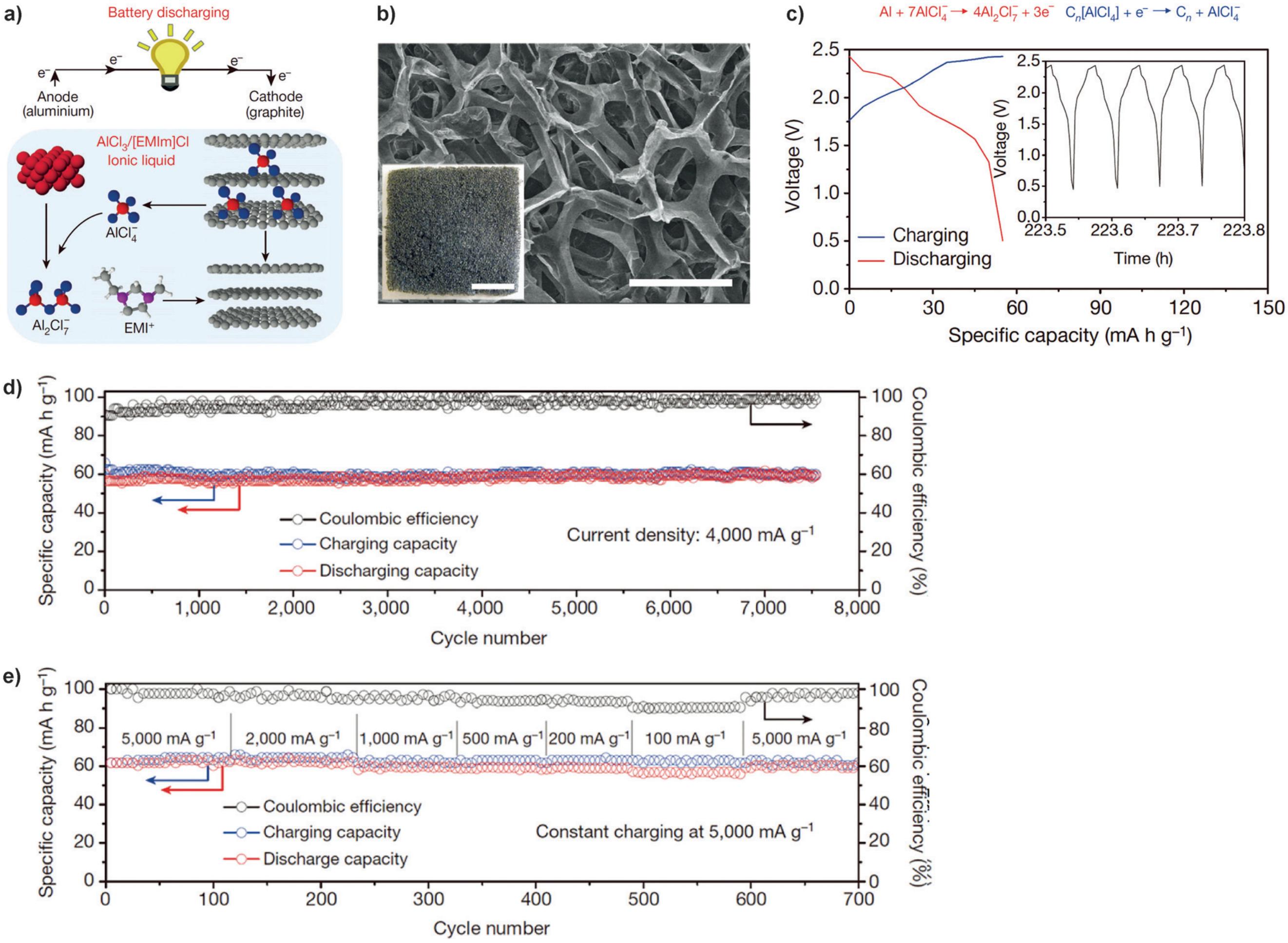

Figure 1. Rechargeable Al/graphite cell. a) Schematic drawing of Al/graphite cell during discharge and proposed reaction mechanism. b) Scanning electron microscopy image showing a graphitic foam with an open frame structure. c) Galvanostatic charge and discharge curves of Al/graphitic-foam pouch cell at 4000 mA g^{-1} current density. d) Long-term stability and e) rate performance tests of Al/graphitic foam pouch cell. The Figure was reproduced with permission from Ref [3].

6000 mA g^{-1}), which were comparable with supercapacitor performance. The high rate performance of the cell could primarily be attributed to the 3D configuration of the graphitic foam cathode. The achievement of such a high rate capability simply by replacing a graphite electrode with a 3D graphitic foam indicates another important finding: The actual kinetics for ion insertion and extraction are considerably faster than expected.

For LIB technology, Dokko and co-workers investigated the electrochemical performance of a single particle of $LiCoO_2$, which is commercially available, using microelectrode techniques.[6] The measured discharge capacity of the 8 μm $LiCoO_2$ was 0.157 nAh at 1 nA current load in the 3–4.2 V potential range, and it retained almost 90 % of its initial capacity at a 20 nA current load, which corresponds to the 127 C rate, as shown in Figure 2 a. Figure 2 b shows the calculated relaxation times, based on the random walk theory, for Li-ion diffusion in representative solid cathodes, which have ionic diffusivities of 10^{-8}–10^{-14}, as a function of particle size. In the figure, the relaxation time of the 8 μm $LiCoO_2$ which has a two-dimensional (2D) diffusion pathway is approximately 16 s, and this is very similar to the experimental data; a discharge at 127 C occurs over a period of approximately 28 s. Therefore, the intrinsic rate performances of commercially available cathode materials for LIBs are considerably faster than that required for practical application in batteries to meet the demands of modern lifestyles. However, current LIBs composed of a lithium-metal-oxide cathode, a carbonaceous material as an anode, and carbonate liquid electrolyte, do not have a comparably high rate performance. This is because of the poor electronic conductivity of the active materials and their electrode architecture; the electronic conductivities of LIB cathode materials, such as $LiCoO_2$, $LiNi_{1-x-y}Co_xMn_yO_2$, $LiMn_2O_4$, and $LiFePO_4$ are 10^{-4}–10^{-14} S cm^{-1}. For example, the cathode electrode is composed of powder-type active materials, a conducting agent, and a polymer binder on the aluminum current collector. To obtain a high energy density, higher mass loading on the current collector, which also means a thicker electrode, is required. However, this leads to an inequality in the electrochemical reaction that varies with distance from the current collector during charging and discharging. More-

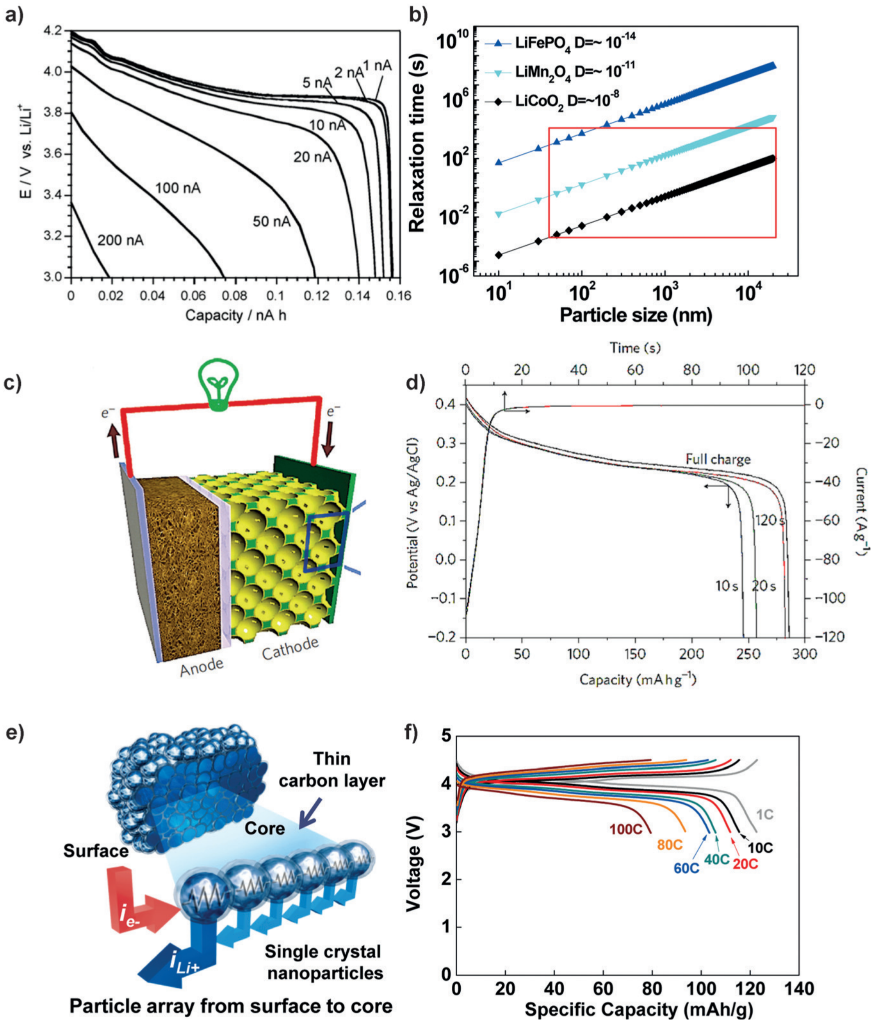

Figure 2. a) Discharge curves of a single $LiCoO_2$ particle (8 μm in diameter) measured at various currents. Prior to each discharge, the $LiCoO_2$ particle was charged up to 4.2 V at a low current of 1 nA. b) Calculated relaxation time for ion diffusions in LIB cathodes as a function of particle size; $\tau = r^2/2D$, $r^2/4D$, and $r^2/6D$ for 1D, 2D, and 3D diffusion, respectively, where r is the particle dimension and D is the diffusion coefficient. c) Schematic representation of a battery containing a bicontinuous cathode. d) Constant potential charge curves of a battery containing a bicontinuous cathode (0.45 V versus silver/AgCl) and 6 C discharge curves after charging at constant potential for the indicated time. The curve labeled "full charge" was charged galvanostatically at 1 C. e) Cross-section and electric-circuit configuration in a nanoparticle cluster. A $LiMn_2O_4$ single crystal is covered with a thin carbon layer that forms an electrical network in the nanoparticle cluster. f) High rate cycle for pouch-type half cells with carbon-coated single-crystal $LiMn_2O_4$ nanoparticle clusters as a cathode (the same charge and discharge rates were used); Voltage profiles as a function of the cycle number with the C rate increasing from 1 to 100 C. Cycles were repeated 20 times for each of the rates and only the first cycles were recorded. Parts of the Figure were reproduced with permission from Refs. [6–8].

over, this inequality also occurs for the active cathode particles, the reaction varying with the distance from the particle surface to the core. Note that the morphologies of commercial cathode materials, such as $LiNi_{1-x-y}Co_xMn_yO_2$, $LiNi_{1-x-y}Co_xAl_yO_2$, and $LiMn_2O_4$, are densely aggregated sub-micrometer-sized particles consisting of primary particles.

In 2011, a 3D electrode developed by Braun and co-workers enabled battery charging within 2 min to be realized. These researchers also demonstrated a general method for creating high-rate rechargeable batteries using a bicontinuous 3D composite battery electrode design. This structure provides efficient and rapid pathways for ion and electron transport, along with very short solid-state diffusion lengths (Figures 2 c,d).[7] In the same vein, we also reported the application of carbon-coated single-crystal $LiMn_2O_4$ nanoparticle clusters as a cathode material for LIBs. These clusters are used to construct a 3D electron and ion pathway in highly dense secondary particles (Figure 2 e).[8] The material can be charged to around 60 % and 84 % of 1 C capacity in 24 and 50 s at 100 and 60 C constant charging, respectively. Moreover, the material exhibits a gravimetric energy density of 300 Wh kg^{-1} of active material (kg_{am}) and delivers a power of 45 kW kg_{am}^{-1} and a volumetric energy of 440 Wh per liter of electrode (L_e), while delivering 68 kW L_e^{-1} of power. All these endeavors aim to achieve rapid intrinsic rate performance of the active material in a practical cell.

In conclusion, the realization of rapid charging capability in rechargeable batteries for use in mobile electronics and electric vehicles, without loss of energy density, has become a primary technical challenge. To achieve rapid progress in this regard, a new electrode design based on 3D electron and ion conducting pathways along with the morphology control of the active materials should be considered.

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