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(54) Title: SHUTDOWN AND REDOX SHUTTLE ADDITIVES FOR BATTERIES

(57) Abstract: A group of shutdown additives are provided in the electrolyte of rechargeable batteries or electrochemical storage or secondary cells. The additives are low molecular weight organic aromatic compounds, and function to prevent overcharging of the cell. Some of the additives also function as redox shuttle additives at less server overcharging conditions. These additives can be used in any rechargeable battery utilizing a non-aqueous or solid polymer electrolyte and a positive electrode which is fully charged at about 4 V vs. Li/Li^+. These include batteries for consumer electronics, communications, power tools, electric vehicles, and load leveling.

Shutdown and Redox Shuttle Additives for Batteries

Related Applications

This application claims priority of Provisional Application Ser. No. 60/160,391 filed 10/18/99, which is herein incorporated by reference.

Government Rights

The United States Government has rights in this invention pursuant to Contract No. DE-AC03-76SF00098 between the United States Department of Energy and the University of California.

Background of the Invention

The invention relates to rechargeable batteries, and more particularly to shutdown additives and redox shuttle additives for overcharge protection in rechargeable batteries.

Reliable and inexpensive overcharge protection for multi-cell lithium (and other) battery stacks is a major obstacle to commercialization of these promising systems in electric vehicles and other high voltage applications. Overcharging not only can reduce rechargeable capacity and cell life, but can also create hazardous conditions. Even moderate overcharging of transition metal oxide cathodes often leads to structural and compositional changes in the oxide matrix which have significant effects on their subsequent cycling behavior.

The redox shuttle approach to overcharge protection employs an electrolyte additive that acts as an internal current shunt when the charging potential exceeds a characteristic onset potential for the additive. The ability of certain organic aromatic compound additives to extend cell life in transition metal oxide lithium solid polymer electrolyte cells under conditions of moderate to severe overcharging has been demonstrated, as illustrated in U.S. Patent 6,004,698 to Richardson et al. Other redox shuttle additives have been reported for both polymer electrolyte, as described by F. Tran-

Van et al., Electrochim. Acta, 44, 2789 (1999), and 4 volt lithium ion cells, as shown in U.S. Patent 5,763,119 to Adachi.

Overcharging of batteries can create hazardous conditions, leading to explosion, fire, and/or release of toxic materials. External protection mechanisms that stop charging when a voltage, temperature, or internal pressure limit is reached are currently in use, but these are subject to failure or abuse (such as using a charger designed for a different battery). Redox shuttle additives provide an internal, automatic overcharge protection mechanism that allows charging current to pass through the cell without overcharging it. The ability of such additives to extend cell life in lithium and lithium ion cells under conditions of moderate to severe overcharging has been demonstrated. However, for many applications, the issue of safety takes precedence over the desire for cell life extension. A mechanism that renders the battery harmless on overcharging is acceptable even though it ends its useful life. Thus "shutdown" additives that achieve this goal are desired. Some of these may act as redox shuttles under moderate overcharge conditions and as shutdown additives when the overcharge conditions are more severe. Both redox shuttle and shutdown additives may be present in the same cell.

Summary of the Invention

Accordingly it is an object of the invention to provide shutdown additives for rechargeable batteries.

It is also an object of the invention to provide shutdown additives for rechargeable batteries that also act as redox shuttle additives at lower overcharge conditions.

It is another object of the invention to provide shutdown additives, which may also act as redox shuttle additives, for rechargeable lithium or lithium ion batteries, particularly 4 V lithium ion batteries.

The invention is a group of shutdown additives for the electrolyte of rechargeable batteries or electrochemical storage or secondary cells, and the rechargeable batteries or electrochemical storage cells with these additives. The additives are low molecular weight organic aromatic compounds, and function to prevent overcharging of the cell. When one or more of the additives is added to the electrolyte of a rechargeable cell, it will

be oxidized at the positive electrode at a potential specific to the additive(s). The product of this oxidation increases the resistance of the cell by means of polymerization, precipitation, electrolyte depletion, chemical reaction, or other mechanism. This prevents further charging of the cell, thereby preventing development of unsafe conditions.

Some of the additives also function as redox shuttle additives at less severe overcharging conditions. When one or more of them is added to the electrolyte of a rechargeable cell, it is oxidized at the positive electrode to its respective radical cation at certain potentials. The cation diffuses through the electrolyte to the negative electrode, where it is reduced to its original neutral state. This allows the additive(s) to transport an electrical charge through the cell without damage to the cell under conditions that would, in the absence of the additive(s), cause it to lose capacity or fail. Under more severe overcharging conditions, the cation transport through the electrolyte is insufficient, and the additives are oxidized at the positive electrode to shut off the cell.

These additives could find use in any rechargeable battery utilizing a non-aqueous or solid polymer electrolyte and a positive electrode which is fully charged at about 4 V vs. Li/Li^+. These include batteries for consumer electronics, communications, power tools, electric vehicles, and load leveling.

Brief Description of the Drawings

Fig. 1 is a cross-sectional view of a rechargeable battery or electrochemical cell.

Fig. 2 is a graph of the onset potentials of two shutdown additives of the invention.

Fig. 3 is a graph of the onset potentials of seven shutdown/redox shuttle additives of the invention compared to two prior art additives.

Fig. 4 is a graph of the onset potentials of seventeen shutdown/redox shuttle additives of the invention.

Detailed Description of the Invention

The invention applies to rechargeable batteries or electrochemical storage cells, e.g. lithium and lithium ion batteries, of the type which are well known in the art, e.g. as

described in U.S. Patents 6,004,698 and 5,763,119, which are herein incorporated by reference. The materials of which the standard parts of the batteries or cells of the invention are made, as well as the configuration of the battery or cell, can be found in these and other references.

Fig. 1 illustrates a battery or cell 12 that is formed within a nonreactive outer case or shell 12 with an optional insulating inner lining 14 inside case 12 that form sidewalls of battery 12. A negative electrode current collector 20 is positioned against one sidewall of battery 12, and a negative electrode 24, which forms the negative electrode material, is positioned next to and in contact with negative electrode current collector 20. Alternatively, negative electrode 24 and negative electrode current collector 20 may form a unitary structure, referred to as negative electrode 24. Similarly, a positive electrode current collector 36 is positioned against an opposed sidewall of battery 12, and a positive electrode 32, which forms the positive electrode material, is positioned next to and in contact with positive electrode current collector 36. Alternatively, positive electrode 32 and positive electrode current collector 36 may form a unitary structure, referred to as positive electrode 32.

Between negative electrode 24 and positive electrode 32 is solid polymer electrolyte 28, which is ionically conducting and also serves as an insulator or separator between the negative electrode 24 and positive electrode 32. In some batteries it may be possible that the electrolyte is liquid. In accordance with the invention, electrolyte 28 includes the shutdown or shutdown/redox shuttle additives of the invention.

The shutdown (SD) and shutdown/redox shuttle (SD/RS) additives of the invention have common structural features including an aromatic ring and electro-withdrawing substituents which give them high oxidation potentials and stabilize the resulting oxidized species. They fall into several structural subcategories. Some additives can be considered to be members of more than one of these subgroups.

Category A: halogenated benzenes and naphthalenes

Category B: substituted methoxybenzenes

Category C: substituted benzodioxoles

Category D: alkyl polyethers

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