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(54) [Title of Invention] Method for processing waste

(57) [Abstract]

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[Problem to be Solved] To provide a practical method for disposing of batteries that has high safety and low environmental impact.

[Means for Solving the Problem] The method for processing waste comprises the steps of dismantling the collected secondary batteries, cleaning the

aforementioned dismantled battery components, heating the cleaned battery components, separating and crushing the active material layers in the electrode components of the heated battery components, immersing the powdered active material layer in an acidic solution to elute the soluble components, separating the insoluble components from the acidic solution, and precipitating and recovering the metal components in the acidic solution.



[Scope of Patent Claims]

[Claim 1] A method for processing waste, comprising a step of dismantling the collected battery, a step of cleaning the aforementioned dismantled parts, a step of heating the cleaned dismantled parts, a step of peeling and separating the active material layer of the electrode elements and crushing it, a step of soaking the powder of the active material layer in an acidic solution to elute soluble components, a step of separating the acidic solution from insoluble components, and a step of precipitating and recovering metal components from the acidic solution.

[Claim 2] A method for processing waste, comprising a step of discharging the collected battery, a step of dismantling the aforementioned discharged battery, a step of cleaning the dismantled parts, a step of heating the cleaned dismantled parts, a step of peeling and separating the active material layer of the electrode elements and crushing it, a step of soaking the powder of the active material layer in an acidic solution to elute soluble components, a step of separating the acidic solution from insoluble components, and a step of precipitating and recovering metal components from the acidic solution.

[Claim 3] The discharge processing step of the recovered battery as described in Claim 2, wherein the discharge processing step of the recovered battery is performed by connecting a conductor of the same material as the electrode collector to one of the battery electrode terminals via a conductive substance, and executing the discharge based on differences in ionization tendency.

[Claim 4] A method for processing waste as described in Claim 2, wherein the recovered battery is dismantled and soaked in an organic solvent selected from alcohol and ketones.

[Claim 5] A method for processing waste as described as described in Claim 1 or Claim 2, wherein the recovery of the battery is performed by passing a resin package enclosing the battery body through multiple rolls with differing rotational speeds to separate the resin package from the battery body.

[Claim 6] A method for processing waste as described as described in Claim 1 or Claim 2, wherein in the step of dismantling the recovered battery, the recovered battery is heated to vaporize and dissipate the internal liquid.

[Claim 7] A method for processing waste as described as described in Claim 1 or Claim 2, wherein in the step of dismantling the recovered battery, an opening is cut that is close to and approximately parallel to the sealing portion on the terminal protruding surface of the recovered battery, or an opening is cut at the corners where each surface intersects vertically.

[Claim 8] A method for processing waste as described in Claim 1 or Claim 2, wherein he dismantled electrode part is heated under a reducing atmosphere at a temperature below 600°C.

[Claim 9] A method for processing waste as described in Claim 1 or Claim 2, wherein the step of peeling and separating the active material layer of the electrode elements and crushing it is performed by placing it on a mesh of 10mm or smaller and applying vibration.

[Detailed Explanation of the Invention] [0001]

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[Technical Field to Which the Invention Belongs] This invention relates to a method for processing waste, particularly concerning methods or recycling techniques for used lithium-ion batteries and nickel-metal hydride batteries. [0002]

[Conventional Technology] In recent years, the demand for batteries for electronic devices such as laptops and mobile phones has dramatically increased. In particular, lithium-ion secondary batteries possess excellent characteristics, including high capacity per unit weight and volume and high voltage, making them an essential secondary battery for miniaturized electronic power sources. Additionally, in California, where air pollution is becoming increasingly severe, a program to promote electric vehicle (EV) sales is expected to begin in 1998. Lithium-ion secondary batteries are being developed for use as these power sources, and a further surge in demand and consumption is anticipated. Consequently, the increase in battery consumption will inevitably lead to large-scale disposal (processing) of batteries, necessitating some form of waste treatment.

[0003] However, since lithium-ion secondary batteries and nickelmetal hydride secondary batteries have only recently been commercialized, practical methods for processing waste are still in a trial-and-error stage.

[0004]

[Problems to be Solved by the Invention] In the aforementioned lithium-ion secondary batteries, while lithium is stable in ionic form, it becomes highly reactive when metalized. Therefore, for safety reasons, it is desirable to centrally recover and dispose of lithium-ion secondary batteries through appropriate methods. That is, because lithium, which exhibits high reactivity when in metallic form, is used in lithium-ion secondary batteries, there is a significant risk of ignition and explosion. Furthermore, if disposed batteries are directly melted or decomposed in an incinerator, the internal pressure may increase, leading to a higher risk of explosion. From a resource perspective, it is also necessary to recover metals such as cobalt and nickel from the electrode elements. On the other hand, since harmful substances may be produced as by-products from fluorine and phosphorus contained in the electrolyte, there is a significant risk of environmental pollution, necessitating more appropriate disposal treatment.

[0005] Moreover, many small batteries, such as the aforementioned lithium-ion secondary batteries, may be used either as standalone units or in structures where multiple battery units are packed in a resin package. When the disposal item is a battery pack, it is crucial to first efficiently separate and remove the resin package so that the internal battery units can be extracted safely, enabling the recovery of useful resources. While one method to extract (separate) the battery units from the resin package involves manual disassembly at the junctions of the package, this approach is not suitable for large-scale disposal processing. Alternatively, mechanically crushing the disposal battery packs collectively, followed by wind separation and specific gravity sorting, could be considered as a mass processing method; however, there is also a risk of sparking due to residual voltage if the battery units are damaged in the process. [0006] In addition, wiring boards are used in many fields, starting with high-performance electronic devices. These wiring boards are typically formed from materials such as valuable metals like copper foil and solder, inorganic substances like flame retardants, and resins, making waste disposal and recovery for reuse challenging. Particularly when harmful substances are present, it is crucial to recover and neutralize these harmful substances without dispersing them while also addressing the difficulty of recovering valuable metals. This is significant both from an environmental perspective and in terms of resource utilization.

[0007] For the recycling of waste wiring boards, organic materials in the wiring board are removed through roasting, and gold from the copper foil and mounted components is recovered using a smelting furnace. This method can handle large quantities and is effective for recovering valuable metals; however, it poses problems from an environmental conservation and recycling standpoint. Specifically, there are concerns about the volatilization of harmful substances contained in the waste, such as lead compounds that have low melting points, and the generation of dioxins due to incomplete combustion. On the other hand, organic and inorganic materials are simply burned and discharged as slag, which has also been proposed for use as aggregate, but its value is lower compared to raw materials, limiting its applications.

[0008] To effectively recycle composite material products containing metals, inorganic materials, and organic substances, it is preferable to separate and sort each material without reducing their inherent energy potential. From the viewpoint of minimizing environmental impact, non-combustion separation technologies have been proposed. For instance, as a preprocessing step for separation, methods involving crushing and grinding the waste wiring boards followed by separation through specific gravity, static electricity, or eddy current sorting have been documented (e.g., Japanese Unexamined Patent Application No. H 7 (1995) - 251154, Japanese Unexamined Patent Application Publication No. H 7 (1995) - 100436, etc.).

[0009] These separation techniques are effective in reducing environmental impact by suppressing the diffusion of harmful substances since they do not rely on combustion; however, because the separation depends solely on crushing, there are limitations to separation efficiency. Not only is the recovery rate of metals low, but a significant amount of metal contaminates the separated resins as impurities, which narrows down the possibilities for resin recycling and application.

[0010] This invention addresses the aforementioned circumstances and aims to provide a practical method for processing waste batteries that is safe and has low environmental impact. [0011]

[Means for Solving the Problems] The invention of Claim 1 comprises a step of dismantling the collected batteries, a step of cleaning the dismantled parts, a step of heating the cleaned dismantled parts, a step of peeling and separating the active material layer of the electrode elements from the heated dismantled parts and crushing them, a step of immersing the powdered active material layer in an acidic solution to elute the acid-soluble components, a step of separating undissolved components from the acidic solution, and a step of precipitating and recovering metal components from the acidic solution.

[0012] Here, the collected batteries include, for example, individual

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lithium-ion secondary batteries, lead-acid secondary batteries, battery packs (packaged batteries) containing circuit substrates, etc. Furthermore, "dismantling" means cutting the outer casing of the individual battery or the battery pack to extract the electrode element components such as the positive electrode, negative electrode, and separator, and if necessary, cutting them into strip-like pieces. The separation of the electrode element components may involve immersing them in a liquid (water, solvent, acidic, or alkaline liquid) after opening the casing of the battery, allowing them to separate by buoyancy, while concentrating and recovering electrolyte components like lithium hexafluorophosphate, ethylene carbonate, and dimethyl carbonate from the liquid used for immersion, and employing magnets to recover metal components floating in the aforesaid liquid.

[0013] Furthermore, the cleaning of the dismantled items can be performed using alcohols such as methyl alcohol or ethyl alcohol, ketones, or alcohol-water solutions. In this case, subsequent drying becomes easier, and peeling later is also facilitated. Additionally, if nitric acid is used as the cleaning solution, it allows for the separation of the substrate from the positive electrode and the binder, thereby eliminating the need for subsequent heating. On the other hand, when an alkali (for example, sodium hydroxide) is used as the cleaning solution, only the aluminum substrate of the positive electrode dissolves, making peeling unnecessary, and thus heating treatment can also be omitted.

[0014] In addition, following this cleaning process, to achieve the separation (decomposition) of the binder from the electrode elements and to remove any remaining solvents or binder components, a heat treatment is performed at a temperature of approximately 40 to 400°C. However, prior to this heat treatment, it is preferable to conduct a vacuum drying process to remove the electrolyte; this enhances the efficiency of subsequent processing.

[0015] Moreover, in this heat treatment, the temperature should be higher than that during electrode manufacturing (generally between 100 to 200°C), but below the temperature at which the fluorine in the binder of the electrode elements (PVdF: 400°C, fluorinated rubber: 300°C) volatilizes. By doing so, only the organic binder components are vaporized, suppressing the generation of harmful substances, while the difference in thermal expansion makes it easier to separate the electrode support and the active material layer.

[0016] Additionally, the peeling and separation of the active material layer from the heat-treated dismantled electrode elements can be preferably promoted by immersing the electrode elements in water and applying external forces, such as ultrasonic vibrations or blowing bubbles. The separation may also involve the decomposition and processing of wiring substrates that constitute part of the battery package. In such cases, it is desirable to structure the insulating substrate as a laminated structure with materials that impose different stress strains, making it easier to yield and cause internal failure under certain stress anomalies.

[0017] The acidic solution used to elute the acid-soluble components from the active material layer powder is intended to dissolve or ionize elements such as lithium, cobalt, and nickel within the

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electrode elements. Generally, examples include hydrochloric acid solutions of 0.1 to 60% or nitric acid solutions of 0.1 to 60%. The separated undissolved components (organic components) are washed with water to remove the acid and collected, while the metal components in the aforementioned acidic solution are either separated and recovered by using ion exchange resins to adsorb (precipitate) the metals or precipitated and then separated and recovered. [0018] The invention of Claim 2 is a method for processing waste that includes the steps of discharging the recovered battery, dismantling the aforementioned discharged battery, cleaning the aforementioned dismantled items, heat treating the aforementioned cleaned dismantled items, peeling and separating the active material layer of the electrode element of the aforementioned heat-treated dismantled items and grinding it, immersing the powder of the aforementioned active material layer in an acidic solution to elute acid-soluble components, separating the aforementioned acidic solution from insoluble components, and precipitating and recovering the metal components in the aforementioned acidic solution. The invention of Claim 3 is an improvement of the method for processing waste described in Claim 2, wherein the discharge process of the recovered battery involves connecting a conductor made of the same material as the electrode current collector to one of the battery electrode terminals via a conductive material, performing discharge based on differences in ionization tendency. This invention adds a step of performing a discharge treatment in advance to safely process the recovered battery for disposal. In other words, if a secondary battery in a charged state is dismantled directly, it could cause a short circuit and potentially ignite organic materials inside the battery; therefore, it is desirable to perform a discharge treatment beforehand. Possible means for this discharge treatment include the following: [0019] (1) For example, if carbon dioxide gas is generated inside the battery due to overcharging and the safety device has activated, cutting off the positive electrode lead, the external part of the battery can be cooled to about 0°C or compressed externally using a pump to liquefy the carbon dioxide gas inside the battery and restore the safety device.

[0020] (2) Using a dedicated battery recovery box equipped with devices capable of executing the aforementioned method (1), the discharge treatment is performed during the transport process of the recovered battery or while the recovered battery is being stored. [0021] (3) Immersing the recovered battery in an electrolyte similar to that in its electrode elements or a non-aqueous solvent to promote natural discharge of the battery. During this immersion, placing electrodes in the immersed electrolyte and connecting a resistor further promotes the discharge.

[0022] ④ If the recovered battery is in an overcharged state or an excessively discharged state, a conductor made of the same material as the electrode current collector is connected to one of the battery electrode terminals via a conductive material, and discharge occurs based on differences in ionization tendency. Here, the electrode current collector is preferably aluminum for the positive side and copper for the negative side, especially when there is a significant difference in ionization tendency.

[0023] For example, when observing the behavior of the negative electrode side connected to a metal immersed in another electrolyte under conditions where the positive and negative electrodes are not

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short-circuited or the battery is not operating, we can see the following phenomena when lithium metal is either deposited on the negative side or not. In the state where lithium metal has deposited on the negative side (overcharged), metal present as ions in the electrolyte elutes from the metal immersed in the electrolyte, causing its weight to increase. Under constant voltage, the flowing electric current gradually decreases, and after some time, the deposition of the aforementioned metal almost stops, resulting in a sharp drop in the electric current value. This phenomenon indicates that, when comparing the standard electrode potentials of metals, the negative side of the secondary battery operates as one half-cell while the piece of metal immersed in the electrolyte acts as another half-cell, thus forming a new battery system.

In the case of an overcharged lithium-ion secondary battery, when lithium uniformly adheres around the copper foil current collector on the negative side, the standard electrode potential becomes lower than that of pure copper. As a result, the copper side connected to the metal immersed in the external electrolyte becomes the positive electrode, allowing electric current to flow. Moreover, the rapid change in electric current occurs because the lithium adhering to the negative side's copper foil current collector detaches, leading to resistance in electric current being dominated by the inherent resistance of copper. Therefore, with a certain voltage, the resistance value increases compared to when lithium was attached. [0024] On the other hand, in the case of a secondary battery in an excessively discharged state, when forced to maintain a constant voltage under conditions similar to the aforementioned overcharge scenario, the metal immersed in the external electrolyte ionizes and acts as a negative electrode, making it easy to confirm the excessively discharged state.

[0025] The invention of Claim 4 is characterized by the method for processing waste described in Claim 2, wherein the recovered battery is dismantled and impregnated with organic solvents such as alcohols or ketones. The invention of Claim 5 stipulates that, in the method for processing waste described in Claim 1 or Claim 2, the recovered battery is one where the resin package enclosing the battery body is separated from the battery body by passing it through multiple rolls with differing rotational speeds.

[0026] This invention is characterized by how the recovered battery is separated from the resin package. Specifically, by passing a battery pack configured to enclose multiple batteries within a resin package through several rolls that have different rotational speeds, shear forces and twisting actions are simultaneously applied by the rotating rollers to break and peel off the resin package, thereby separating the enclosed battery body. The gap between the rolls must be set to be less than the overall thickness of the battery pack to ensure that sufficient force is transmitted to the resin package. At the same time, it must be set to be greater than the thickness of the battery body to avoid damaging it. Therefore, when applying this separation means, it is preferable to sort the battery packs by shape in advance. Moreover, if the batteries to be processed are mixed types with varying thicknesses and shapes, it is desirable to design the device configuration in advance to accommodate batteries of different thicknesses.

[0027] For example, one can establish multiple pairs of rolls with

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