



Radiation effects on the electrode and electrolyte of a lithium-ion battery



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H I G H L I G H T S

- Gamma radiation effects on cathode or electrolyte of Li-ion batteries were studied.
- Radiation leads to capacity fade, impedance growth, and premature battery failure.
- Electrolyte color changes gradually after initially receiving radiation dose.
- Polymerization and HF formation could be the cause of the latent effects.

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The performance degradation and durability of a Li-ion battery is a major concern when it is operated under radiation conditions, for instance, in deep space exploration, in high radiation field, or rescuing or sampling equipment in a post-nuclear accident scenario. This paper examines the radiation effects on the electrode and electrolyte materials separately and their effects on a battery's capacity loss and resistance increase. A ⁶⁰Co irradiator (34.3 krad/h) was used to provide 0.8, 4.1, and 9.8 Mrad dose to LiFePO₄ electrodes and 0.8, 1.6, and 5.7 Mrad to 1 M LiPF₆ in 1:1 wt% EC:DMC electrolytes. This study shows that the coin cells assembled with irradiated components have higher failure rate (ca. 70%) than that of control group (ca. 14%). A significant battery capacity fade post irradiation was observed. The electrolyte also shows a darkened color a few weeks or months after irradiation. The discovery of this latent effect may be significant because a battery may degrade significantly even showing no sign of degradation immediately after exposure. We investigated electrolyte composition by Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, and nuclear magnetic resonance spectroscopy prior and post irradiation. Polymerization reactions and HF formation are considered as the cause of the discoloration.

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1. Introduction

Rechargeable lithium ion batteries (LIBs) are widely utilized as the power source for large scale industrial and automotive applications, as well as portable devices. In particular, this technology is being considered as either the main or alternative power source in unmanned aircraft, satellites, spaceships and probes for outer space

exploration. LIBs are also commonly found in robots including those performing rescue and sampling missions in highly radioactive environments, such as those used in a post-nuclear accident site or in radioactive hot cells. A lingering concern when using lithium ion cells in such radioactive extreme conditions lies in the ability to retain acceptable performance after radiation exposure. The intense radiation environment may degrade the properties of the electrode and electrolyte materials quickly, significantly reducing the battery performance. The latent effects due to radiation exposure can also result in long term battery failures.

Previous studies have investigated the radiation effects on LIBs at the full cell level with varying observations. For example,

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Ratnakumar et al. [1] reported a good resistance to gamma radiation up to 25 Mrad on a LIB with a graphite anode and nickel cobalt oxide cathode, while Ding et al. [2] observed 50% capacity loss induced by gamma radiation with LiCoO₂ cathode at dose level of 14.4 Mrad. Qiu et al. [3] also showed performance degradation of LIBs with LiCoO₂ cathode at 10 Mrad. Several authors have indicated that decomposition of the electrolyte (1 M LiPF₆ in EC/DMC 1:1 wt% or vol%) in commercial cells may occur under high dose gamma radiation [2,4,5]. However, it is often difficult to correlate full cell performance degradation studies to the components that are most affected by radiation.

To understand the radiation effects on individual battery components and thus to guide the design of battery components with sufficient tolerance to radiation, it is necessary to study the separate radiation effects imposed on the electrode and electrolyte materials. For example, the anode of a commercial LIB is typically made of graphite, which is known to be relatively unaffected by radiation damage (for instance, graphite is used in nuclear reactors as a moderator). However, the graphite in a LIB may be lithiated, where Li is intercalated into the graphite sheet. During the Li intercalation process, new chemical species may be formed on the electrode interface, which can be prone to radiation damage, ultimately compromising the ability of graphite to intercalate and deintercalate Li ions. LiFePO₄ was used as the cathode material in this case, since it is a common electrode material used in power tools and motive power applications due to its high capacity (170 mAh/g) and high rate capabilities [6,7]. LiFePO₄ is also inexpensive and the material is environmentally benign [8] compared to those containing cobalt, nickel, or manganese in other types of electrode. The excellent Li reversibility in LiFePO₄ is due to the relatively similar structures of LiFePO₄ and FePO₄ [8]. Even small changes to the crystal structure may result in the decrease of Li reversibility and thus the loss in battery capacity and cycle performance. The organic electrolyte and electrolyte additives are believed to be most vulnerable to radiation due to chemical bond breakdown caused by gamma radiolysis. It has been found that the dimethyl carbonate (DMC), a major component in commercial battery electrolytes, will decompose significantly under radiation when moisture is present [4]. However, it is still unknown as to the effects of radiation on a dry dimethyl carbonate.

This study investigates the effects of gamma radiation on a commercial cathode and electrolyte typically used in a commercial lithium ion cell. The electrodes and electrolytes were exposed to a ⁶⁰Co source at 34.3 krad/h at The Ohio State University's Nuclear Research Reactor Laboratory. LiFePO₄ cathodes (thickness of 1.5 mm; diameter of 24 mm) and electrolytes were irradiated separately. After irradiation, the components were fabricated into a series of coin cells for capacity and resistance characterization. The coin cells containing irradiated electrodes, or irradiated electrolytes were compared to a series of control samples fabricated from the same batch of electrodes and electrolytes without exposure to radiation. In addition to battery performance measurements, X-ray diffraction of the cathode material and spectroscopic studies on the electrolyte were also conducted to investigate the phase or structural changes with exposure to radiation. The structure of the electrode was characterized using X-ray diffraction (XRD) prior to and post-irradiation. Electrolytes were transparent immediately post irradiation, but were found to have significant color change after long term storage. Optical and nuclear magnetic resonance (NMR) were applied to the electrolyte to investigate the cause of the color change.

2. Experimental

The experiment started with the preparation of the materials

and the irradiation scheme shown in the flowchart in Fig. 1(a). Pristine cathode material in this study was retrieved from fresh A123[®] commercial prismatic Li-ion batteries (A123 Systems, LLC), consisting of carbon-coated LiFePO₄. The active material was made of by mixing LiFePO₄ with carbon black, graphite and polyvinylidene fluoride (PVDF) binder on an aluminum current collector. The thickness was estimated to be 150 μm. The LiFePO₄ laminate was cut into 24 mm diameter disc. The cathode was cleaned using dimethyl carbonate (DMC) and dried at 75 °C for 12 h. The electrolyte used in this study was a commercial electrolyte, Selectlyte™ (1.0 M LiPF₆ in 1:1 w/w of ethylene carbonate: dimethyl carbonate, EC:DMC). Both cathodes and electrolytes were stored in an Ar atmosphere prior to assembly to avoid exposure to air and moisture.

Prepared samples were sealed in glass bottles with Parafilm[®] wrapped around the cap and placed in two ziplock-bags inside the glove box. The ziplock-bag was filled with argon gas for transportation and irradiation. Cathodes (supported on an Al current collector) and electrolyte samples were irradiated in a sealed glass vials separately. The glass vials are visual transparent and have a wall thickness of ~1.1 mm, and their attenuation to the ⁶⁰Co gamma rays (average energy 1.25 MeV) is negligible. The cathode samples were irradiated by a ⁶⁰Co source (34.3 krad/h) for 1, 5, and 12 days, corresponding to 0.8, 4.1, and 9.8 Mrad, respectively. The electrolyte samples were irradiated with the same source for 1, 2, and 7 days, corresponding to 0.8, 1.6, and 5.7 Mrad, respectively.

After irradiation, the cathode and electrolyte were brought back to the battery fabrication facility and assembled into coin cells in an argon gas filled glove box. The coin cell assembly is composed of a stainless steel case (CR2032), a stainless steel spring and spacer, a lithium metal counter and reference electrode, a counter electrode, a polymeric separator, and 1 M LiPF₆ in EC/DMC (1:1) electrolyte. Each coin cell had either the cathode or the electrolyte pre-irradiated, while the other components were not irradiated (Fig. 1(b)).

Seven samples were prepared as the control group and characterized under the same conditions as those in the irradiated groups. Another purpose of preparing a large group control sample is to provide an uncertainty baseline due to cell-to-cell variation and the fabrication process.

To minimize potential aging of the irradiated materials, the coin cells were assembled immediately after radiation and mounted in the battery cycler. The testing cycle was completed within an average of 5 days for each cell. Three charge-discharge formation cycles (from 3.6 V to 2.8 V) with one at C/25 rate followed by two at C/10 rates were applied to all cells, including the control group. Immediately after the formation cycles, the capacity was measured using a constant current-constant voltage (CCCV) charge/discharge protocol. Firstly, the cells were brought to 3.6 V by a C/2 current, followed by a constant potential hold at 3.6 V. After a 30-min rest, a constant current discharge of C/10 was applied until the voltage reached to 2.8 V. Similarly, a constant potential hold at 2.8 V was sustained until the discharge current dropped under the C/20 limit (~0.075 mA). Resistance was monitored when charging and discharging occurred at different depths of discharge. Briefly, after being brought to full charge, the cells were discharged to around 80%, 60%, 40%, and 20% of full charge. After a rest of 40-mins following the discharge stages, positive and negative current pulses of C/6 rate were applied for tens of seconds when the cells were maintained at those state of charge (SOC) levels. The material preparation, irradiation, cells fabrication, and testing were all conducted under the room temperature.

XRD study was conducted on non-irradiated and irradiated electrodes using Rigaku MiniFlex 600 and a Rigaku Smartlab. Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer) and

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