

Evaluation of NP-MnFe₂O₄ as an Efficient Nanocatalyst for Air Cathode and 1-Octyl-3-methyl Imidazolium Hexafluorophosphate [Omim][PF₆] as a Green Electrolyte in Rechargeable lithium-Air Battery

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Abstract

A simple, new and low-cost design of Li-air battery was introduced. An effective synthesized nanocatalyst for modifying of air cathode, filter paper as a simple separator and a conductive ionic liquid namely 1-Octyl-3-methyl imidazolium hexafluorophosphate abbreviated [Omim][PF₆] as a non-aqueous and green electrolyte in battery were used. The MnFe₂O₄ nanoparticles (NP-MnFe₂O₄) which consisting of transition metal-metal oxide components was synthesized in our laboratory. High discharge capacity, non-flammability of electrolyte, high reversibility, long lifetime and low over potential were observed in electrochemical tests of the battery. Synthesized nanocatalyst was characterized using XRD, FTIR and SEM techniques. XRD results show that a nanocatalyst have a particle sizes of 16-28 nm that distributed on cathode uniformly and performance of battery was improved to more than 1000 cycles compared to battery without any catalyst. The discharge capacity at current density of 0.2 mA cm⁻² and charge potential range of 2.0-4.2 V for battery with catalyst/green electrolyte and without catalyst/common organic electrolyte were 3391 and 1012 mAh g⁻¹, respectively. Furthermore, the usage of an ionic liquid as electrolyte leads to the increase the safety and lifetime of battery. Because of used electrolyte have high boiling point amount (>350 Celcius), so if it released to the environment due to the destruction or life expires of battery, don't seriously damage to the environment because it is not easily evaporated.

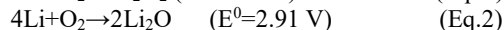
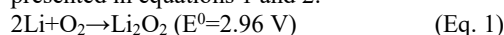
Keywords

Li-air Battery; Simple Design; Nano-Catalyst of MnFe₂O₄; Ionic Liquids; Green Electrolyte; High Discharge Capacity.

1. INTRODUCTION

The Li-air batteries are the more promising rechargeable batteries rather than other energy-storage systems such as Li-ion batteries, because having much higher energy densities [1,2]. They are the most possible candidates to meet the need of long-ranged electrified systems with high energy densities and long lifetime [3,4]. The rapid depletion of finite fossil fuels and global warming due to the CO₂ emission make the development of the clean (or green) energy storages a worldwide imperative. Among the all energies saving systems, the Li-air batteries have the highest theoretical specific energy (about 11140 Wh kg⁻¹) compared to gasoline (33700 Wh/ gallon) [5,6]. Furthermore, the Li-air batteries could be practically give gravimetric energy of three times or greater than of the Li-ion batteries [7-10]. At firstly, Abraham and Jiang reported the non-aqueous electrolytes in the Li-air batteries [11-18]. A simple design for the non-aqueous Li-air batteries contains lithium metal as an anode, a supported conductive porous carbon paper as a cathode, an anode/cathode separator and a

suitable electrolyte as an electrical connecto. The likely spontaneous discharge or oxygen reduction reactions (ORR) (after set up of the battery) are presented in equations 1 and 2.



In practice, discharge and charge potentials for most of the Li-air batteries are approximately 2.60 V and 4.0 V, respectively. At charge process, the oxygen evolution reaction (OER) process (equation 3) was occurred [19-21] and the overpotential (difference) between the discharge and charge processes severely reduces the cycle efficiency of the batteries.



Furthermore, the discharge products *i.e.* Li₂O₂ or Li₂O are not soluble in organic electrolytes and consequently deposit on the porous carbon paper in cathode. This undesired change, increases the polarization and blocks the further intake of oxygen with cathod, which leading to decrease in the cycle performance and lifetime of battery. There are many other obstacles that must be overcome including the instability and volatility

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of the organic electrolytes due to low boiling point, corrosion of lithium metal (oxidation) in anode owing to direct intake of oxygen and the air breathable separators. ORR/OER processes during discharge/charge are taken place on air cathode sluggishly in Li⁺-containing aprotic electrolytes without catalyst [22], which influence the properties of the Li-air battery significantly. To increase the capacity, capability and decrease the overvoltage in the Li-air batteries, the catalysts should be used to accelerate the ORR and OER processes [23]. Excellent catalytic activity and stability of the electrolyte are the requirements parameters for the catalyst of ORR and OER processes. Noble metals and alloys [24] and some transition metal oxide [25] extremely have been used as catalysts in air cathode. A study has evaluated the effect of several catalysts on the properties of the Li-air batteries and it was found that the catalysts have a low effect on the discharge voltage, and high effect on specific capacity, charge voltage and cyclic behavior. Nanoparticles are more appropriate for ORR and OER processes due to having a large surface area compared to bulk ones [26]. For instance, alpha-MnO₂ nanowires as the catalyst increase the capacity of Li-air battery to 3000 mAh g⁻¹. In another report, the mixed Au-Pt nanoparticles in cathode have effective catalyst behavior, where Au and Pt particles were targets for ORR and OER process, respectively [27]. It is generally believed that the catalysts could be increase the discharge potential, decrease the necessary charge potential and thus ultimately improve the cyclic performance. Therefore, the catalysts are strongly necessary to improve the performance of the rechargeable Li-air batteries. The ionic liquids (ILs) are interesting conductive compounds for many applications in the soft-matter systems from electrochemistry to energetic materials. Certain highlighted properties containing high boiling point, low melting point, wide liquid range, low toxicity, non-flammability, good extractability/viscosity and negligible vapor pressure have encouraged researchers to explore the usage of the ILs to replace with volatile organic solvents (VOCs) in various applications [28]. Because of low toxicity of ionic liquids, they have not any hazardous effects on the environment [29]. The room-temperature ionic liquids (RTILs) are being considered as a replacement for many usual and hazardous solvents (organic or inorganic) in the various applications [30,31]. The ionic liquids could be used as an electrolyte in Li-air batteries because they are conductive materials with low toxicity and non-flammability properties [32,33]. The common used electrolytes in the Li-air batteries

are divided into aqueous and non-aqueous electrolytes, which non-aqueous ones are more appropriate in the Li-air batteries [34-38], because they can not oxidize anode and does not be evaporate easily. Some common organic solvents are used as electrolytes in Li-air batteries including carbonic esters (such as ethyl- and methyl carbonate), ethers and alkanes which significantly suffer from water absorbability, volatility, viscosity, conductivity, oxygen solubility and diffusion rate [39]. However, the solvent volatility is considered as a main problem in the organic electrolytes especially in the Li-air batteries having the semi-open system that oxygen continuously flows (inter or exit) therein. Decreasing of the battery power due to the volatility of the electrolyte in the process can be effectively prevented by replacement with the stable materials such as ionic liquids. Furthermore, the reaction of water (in air as moisture) with the lithium can be removed by use a non-aqueous ionic liquid as electrolyte [40]. The conductivity of the Li⁺ ions is relatively low in the non-aqueous electrolyte because of its low solubility but it is highly soluble in the ionic liquids [41,42]. The electrolyte not only should be conduct a Li⁺ ions, but also should effectively protect the lithium anode from direct contact with oxygen. If the electrolyte acts well, partly dissolve the discharge product *i.e.* lithium oxide improve the discharge performance and the stability of the cycle operation.

In the present work, the MnFe₂O₄ nanoparticles were synthesized as an efficient catalyst and loaded on carbon paper as the air cathode. The Li-air battery was then assembled and the filter paper was used as a separator layer due to the simplicity and a suitable non-aqueous ionic liquid was used as an electrolyte.

2. EXPERIMENTAL

2.1. Catalyst synthesis and characterization

The MnFe₂O₄ nanoparticles were synthesized by co-precipitation method that reported in the literature [43,44]. At briefly, 50 mL of a solution containing manganese (II) chloride monohydrate (0.02 mol) and ferric (III) chloride (0.04 mol) was mixed at room temperature. The pH of the mixture was adjusted to 9.0 by adding the NaOH solution (0.1 mol L⁻¹) and then the solution was stirred vigorously for 45 min. Next, the mixture was heated at 90 °C for 2 h. After cooling, the mixture was filtered to discard any pollutants and unreactive reagents. The obtained solid particles repeatedly washed with distilled water for several times and then, the resulted product was dried at 110 °C for 2 h. The structure of the prepared catalyst was analyzed using a Bruker D8

advanced laboratory X-ray diffractometer equipped with a $\text{CuK}\alpha$ as a radiation source ($\lambda=1.5418 \text{ \AA}$). The XRD patterns were analyzed using X'pert Highscore Plus software and the graphs were drawn in Origin Lab version 2016 software. To detect the functional group of the catalyst, FTIR (Perkin Elmer, Spectrum GX) experiment was used and spectra were taken over the $400\text{--}4000 \text{ cm}^{-1}$ range by the co-addition of 64 scans with a resolution of 4 cm^{-1} . To evaluate the structure and morphology of the synthesized catalyst, SEM (VEGA, TESCAN-LMU) technique was employed and images were taken in high vacuum mode and with a 20-kV accelerating voltage.

2.2. Electrolyte preparation

The ionic liquid of 1-Octyl-3-methyl imidazolium hexafluorophosphate in abbreviated $[\text{Omim}][\text{PF}_6]$ as a non-aqueous electrolyte was synthesized in our laboratory. At Briefly, equal molar of 1-methylimidazole and 1-chlorooctane were added to a three-necked round-bottomed flask equipped with a reflux condenser, magnetic stirrer and a gas inlet. The mixture was heated under nitrogen gas at $70\text{--}75 \text{ }^\circ\text{C}$ with stirring for 72 h. The progress of the reaction was evaluated by thin layer chromatography (TLC). The obtained viscous slightly yellow liquid was cooled at room temperature and ethyl acetate was added to it along with the mixing to remove the impurities and unreacted reagents. The upper ethyl acetate was decanted and the washing was repeated for three times using fresh ethyl acetate. Finally, the remained ethyl acetate was removed by heating at $50\text{--}60 \text{ }^\circ\text{C}$ under vacuum and the water-miscible ionic liquid $[\text{Omim}][\text{Cl}]$ was obtained. To produce the water immiscible $[\text{Omim}][\text{PF}_6]$, the $[\text{Omim}][\text{Cl}]$ ionic liquid was diluted in the methanol/distilled water (50:50) and transferred to a flask and a solid powder of NH_4PF_6 in an equal molar ratio was added. After stirring for 2 h, two phases were formed. The upper phase containing acidic aqueous solution layer was decanted and the lower phase containing $[\text{Omim}][\text{PF}_6]$ was washed with the deionized water until the washing solution was no longer acidic. The $[\text{Omim}][\text{PF}_6]$ obtained was dried under vacuum. To use $[\text{Omim}][\text{PF}_6]$ as an electrolyte, the purified $[\text{Omim}][\text{PF}_6]$ was mixed with the LiPF_6 salt to increase the conductivity and concentration of the Li^+ ion.

2.3. Air cathode preparation

The air cathode was prepared as following procedure: At first, a carbon paper in a disc shape was cutted in the area of 7.1 cm^2 and a three-components slurry containing catalyst, binder, carbon black (with the weight ratio of 22:12:68

mg, respectively) was sprayed onto it at the distance of about 0.5 meter from sprayer using a flow of condensed air (made in Iran). Beforehand, three components slurry were prepared in the mixture of 2-propanol and water in the ratio of 80:20 mL. Then, the slurry dried onto the carbon paper at room temperature and after evaporation of the solvents, was used as air cathode in the battery.

2.4. Anode preparation

For preparation the anode, the granular lithium covered by a supported oil was used. An aluminum sheet (with the area of 7.1 cm^2 and the diameter of 3 mm) was used as a supporter and a current collector. A few grains of the granular lithium was pressed exactly under the pressure of 10 bar by a press device (Baspar-Novin of Isfahan Co., Iran) to form a uniform layer of lithium onto the Al-support. To avoid lithium oxidation, the lithium surface was covered by two layers of the Whatman filter paper impregnated in the electrolyte and then was pressed. Accordingly, the anode of the battery was simply prepared and located within the structure of the battery.

2.5. Assembly of the battery

The battery cell was designed by our team (Fig. 1). The designed cell possesses several components that can be divided into three main categories.

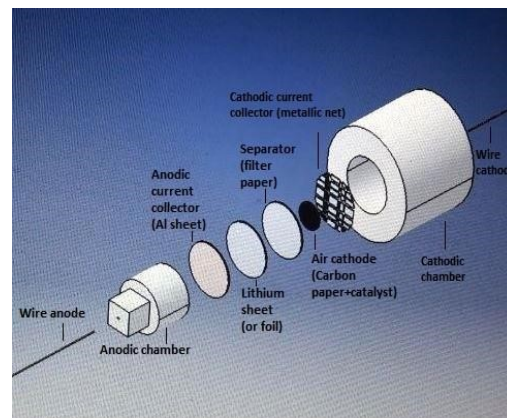


Fig. 1. Components structure of the designed Li-air battery

Part (I) contains a wire connected to the cathode, cathodic chamber, cathodic current collector and air cathode; part (II) contains a cathode/anode separator. We used the Whatman filter paper as an effective, simple and new separator because it has suitable properties such as stability, high porosity and penetrability. Then, it was dipped within an electrolyte. Part(III) contains a lithium sheet, an anodic current collector and a wire connected to the anode. The air cathode was

provisory prepared by soaking the carbon paper sheet into the slurry mixture of three components containing the catalyst, polytetrafluoroethylene (PTFE) as the binder and Kitchenblack carbon (KB) with the weight ratio of 22:12:68 mg, respectively.

2.6. Electrochemical measurements

The battery performance was tested between potential of 2.0 from 4.2 V at a constant current of 0.1 mA cm⁻² in room temperature, using Kimia State 126 multi-channel battery testing system (Made by China). Before each test, the battery was rested for 2 h to reach the equilibrium of oxygen concentrations and moisture of electrolyte.

3. RESULT AND DISCUSSION

3.1. Evolution of the structure and morphology of the catalyst

X-ray diffraction pattern for the synthesized catalyst (NP-MnFe₂O₄) was the same with several works [38,39]. Results in Fig. 2 indicated the Fe-O and Mn-O oxides exist mainly in the MnFe₂O₄ structure. The Fe and Mn components were as a complex (MnFe₂O₄) and had 2θ diffraction peaks at 18.1°, 29.7°, 35.0°, 42.5°, 52.8°, and 61.9° and consequently, spinel structure of MnFe₂O₄ was verified. The XRD data clearly confirmed the crystalline phase of ferrite (MnFe₂O₄) very close to the JCPDS No. 89-4319. For the synthesized MnFe₂O₄, the most intensive lines (311) and (440) were observed in the diffraction peak at 35° and 61.9°. The XRD pattern shows that the prepared nanoparticles were in a cubic structure.

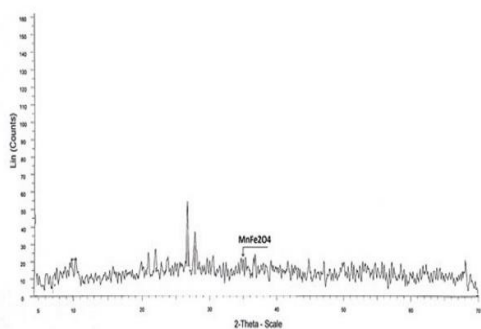


Fig. 2. XRD spectrum of synthesized nanocatalyst.

In addition, it was found from Fig. 3a-c that (scales of 10 μm, 1 μm, and 200 nm) the NP-MnFe₂O₄ sample appears to be a combination of nanoparticles with particles size between 16 and 28 nm, which aggregate with each other to form the film-like morphology. Furthermore, uniform

distribution of the porosity in the particles is one of the main advantages of the synthesized catalyst. In cathode, high surface area of the catalyst is necessary to save discharge products *i.e.* Li₂O₂ or Li₂O. Furthermore, high porosity of cathode cause to increase the penetration of oxygen during discharge/charging processes. The SEM of catalyst shows that the cathode has all mentioned properties simultaneously.

FTIR analysis results show the vibrational frequencies of the various chemical bonds in the MnFe₂O₄ nanoparticles. The results clearly show two absorption bands at 589 cm⁻¹ and 451 cm⁻¹ relevant to the vibrations of Fe-O or Fe-O-Fe bonds, respectively, which are indicative of the formation of spinel ferrite structure. Furthermore, the normal mode of vibration in the tetrahedral cluster at 589 cm⁻¹ is higher than that of the octahedral cluster (447 cm⁻¹).

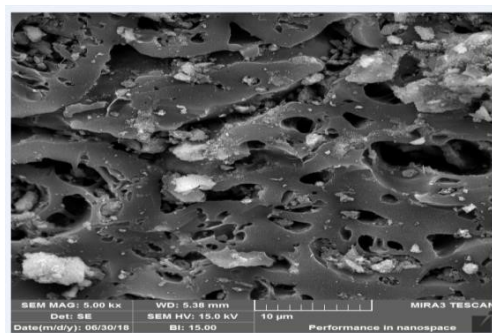


Fig. 3.a. SEM image of the catalyst in 10 μm scale.

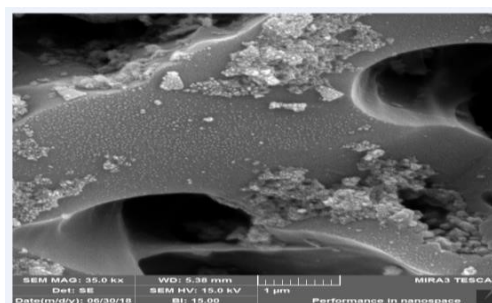


Fig. 3.b. SEM image of the catalyst in 1 μm scale.

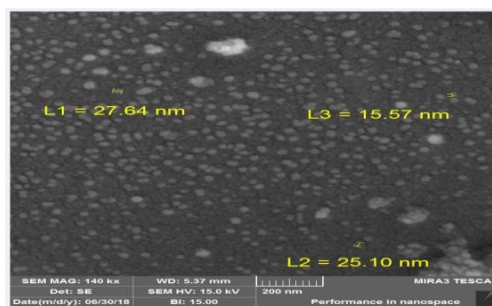


Fig. 3.c. SEM image of the catalyst in 200 nm scale.

3.2. Electrochemical performance of the battery in the presence and absence of the catalyst

The effect of the catalyst on the discharge performance of the Li-air battery was examined. The discharge voltage and capacity of the battery were tested in the presence and absence of the catalyst. As shown in Fig. 4, the air cathode with the catalyst of NP-MnFe₂O₄ (in the electrolyte LiPF₆/[Omim][PF₆]) shows a discharge capacity of 3391 mAh g⁻¹. Furthermore, in the cathode without the catalyst (in the electrolyte of LiPF₆/Dimethyl carbonate) the discharge capacity is 1012 mAh g⁻¹ when the constant current density of 0.2 mA cm⁻². It is clear that the battery with the catalyst shows a capacity of approximately three times compared to the catalyst-free one. The discharge voltage of the cathode is about 2.2 V and 2.0 V, at the presence and absence of the catalyst, respectively. The capacity and the voltage difference (about 0.2 V) confirm the electro catalytic activity of the nano-MnFe₂O₄. The amount of the over potential in the battery is decreased slightly when the catalyst is used in the battery.

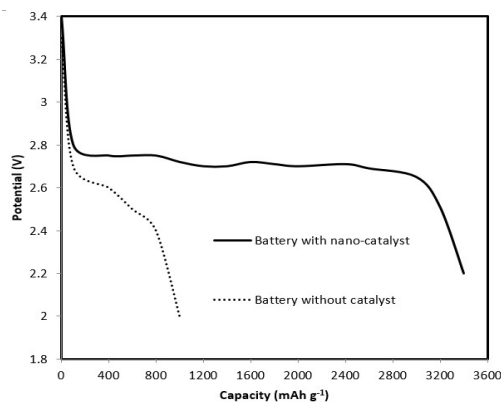


Fig. 4. Discharge characteristic of the Li-air battery at a current density of 0.2 mA cm⁻².

3.3 Charge/discharge cycling

There are some important reasons for the usage of catalyst and ionic liquid (as a suitable electrolyte) such as increase of the charge/discharge cycling and safety following lifetime of the battery, respectively. The obtained charge/discharge curves are shown in Fig. 5a-b. Results indicate that the number of the charge/discharge cycling is increased more than 1000 cycles when the catalyst and LiPF₆/[Omim][PF₆] as electrolyte are used, but it is decreased up to 3 cycles for battery without any catalyst and ionic liquid electrolyte (in the last case a common electrolyte such as LiPF₆ salt was dissolved in dimethylcarbonate (DMC) as solvent). In cycling test curves, the vertical and horizontal axes show the potential (in mV) and the time of the cycling period (in second), respectively.

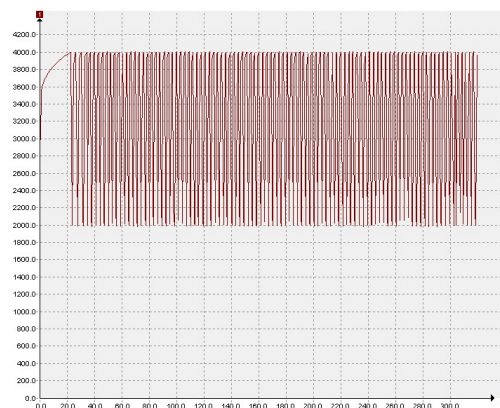


Fig. 5 a. Charge/discharge cycling curve for the Li-air battery in the presence of the nano-MnFe₂O₄ catalyst and LiPF₆/[Omim][PF₆] electrolyte.



Fig. 5 b. Charge/discharge cycling curve for the Li-air battery in the presence of the LiPF₆/DMC electrolyte and in the absence of the catalyst.

We used an ionic liquid namely 1-Octyl-3-methylimidazolium hexafluorophosphate [Omim][PF₆] as the non-aqueous electrolyte, because the boiling point of the electrolyte is high (more than 350 °C). Therefore, the hazard of evaporation, flammability and loss of electrolyte is decreased and the safety of the battery and its regular function is increased during the working of the battery. For this purpose, we compared the battery performance under two different conditions. At first, the battery was designed according to the mentioned structure in Fig. 1 with all components and air cathode along with the catalyst (NP-MnFe₂O₄) and the ionic liquid electrolyte (LiPF₆/[Omim][PF₆]). After 1 month testing of the battery (every day about 4 h charging/discharge process and 1000 cycles), it was not observed any decrease in the discharge capacity and voltage. Alternatively, in the second conditions, we changed the electrolyte of the battery to LiPF₆/DMC and did not use any catalyst. After 17 days, the amount of the discharge capacity was decreased to 484 mAh g⁻¹ and an irregular cycling reversibility behavior was

observed for the battery. The behavior of the battery in the last conditions can be attributed to the lack of the catalyst and evaporation of the organic solvent. In addition, the using of the ionic liquid results in an increase in the safety of the electrolyte as well as the performance of the battery.

4. CONCLUSION

The application of MnFe₂O₄ nanoparticles as a catalyst in the Li-air battery is reported for the first time. The nanoparticles of catalyst were sprayed on the air cathode electrode and then put in Li-air battery. The cathode was modified using nanocatalyst which shown catalytic activities on ORR and OER reactions. By using the NP-MnFe₂O₄ as catalyst and mixture of LiPF₆+ [Omim][PF₆] as electrolyte, the discharge specific capacity of battery reached to 3391 mAh g⁻¹. Use of ionic liquid as a conductive electrolyte connector led to an incensement in the solubility of LiPF₆ between anode and cathode. Furthermore, the usage of [Omim][PF₆] ionic liquid as a non-aqueous electrolyte not only has not any negative effect on the lithium metal, but also prevent the formation of unwanted discharge product *i.e.* LiOH. It also increases the safety of the battery because of its high boiling point (more than 350 °C). This ionic liquids and same structure compounds have high boiling point amount and low vapor pressure, so when the battery life expaire or break it down, released electrolyte contains to the environment at ambient temperature does not evaporate easily and does not damage to the environment. The designed battery has several advantages such as high cycling charge/discharge capability, high discharge capacity, high safety and high lifetime.

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بررسی نانوذرات NP-MnFe₂O₄ به عنوان کاتالیست مؤثر برای کاتد هوا و الکترولیت سبز ۱-اکتیل-۳-متیل ایمیدازولیوم هگزاfluوروفسفات [Omim][PF₆] در باتری قابل شارژ لیتیم-هوا

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چکیده

یک طراحی ساده، جدید و کم هزینه برای باتری لیتیم-هوا معرفی شده است. یک نانوکاتالیست کارا و مؤثر برای اصلاح کاتد هوا، کاغذ صافی به عنوان جداکننده ساده و مایع یونی رسانای ۱-اکتیل-۳-متیل ایمیدازولیوم هگزاfluوروفسفات با نام اختصار [Omim][PF₆] به عنوان الکترولیت غیر آبی و سبز (دوست دار محیط زیست) باتری بکار برده شده است. نانوذرات MnFe₂O₄ شامل اکسید فلزات-فلزات واسطه بوده و در آزمایشگاه تحقیقاتی ما سنتز شده است. ظرفیت دشارژ بالا، الکترولیت غیر قابل اشتعال، برگشت پذیری بالا، طول عمر زیاد و اورولتاژ کم در تست‌های الکتروشیمیایی باتری مشاهده شد. نانوکاتالیست سنتز شده بوسیله تکنیک‌های XRD، FTR، SEM و مشخصه یابی شد. نتایج XRD نشان داد که نانوکاتالیست دارای اندازه ذرات بین ۱۶-۲۸ نانومتر بوده که به طور یکنواخت بر روی کاتد پراکنده شده و کارایی آن به بیش از ۱۰۰۰ سیکل در مقایسه با باتری بدون کاتالیست افزایش یافته است. ظرفیت دشارژ در دانسیته جریان ۰.۲ mA cm⁻² و پتانسیل شارژ ۲/۰ تا ۴/۲ ولت برای باتری دارای کاتالیست/الکترولیت یونی و بدون حضور کاتالیست/الکترولیت آلی به ترتیب برابر ۱۰۱۲ mAh g⁻¹ و ۳۳۹۱ حاصل شد. علاوه بر این، استفاده از مایعات یونی به عنوان الکترولیت باعث افزایش ایمنی و طول عمر باتری شده است. بخاطر اینکه الکترولیت مورد استفاده دارای نقطه جوش بیشتر از ۳۵۰ درجه سلسیوس می‌باشد، بنابراین اگر به دلیل پایان یافتن عمر باتری یا تخریب آن وارد محیط زیست گردد، به راحتی تبخیر نمی‌گردد.

واژه‌های کلیدی

باتری لیتیم-هوا؛ طراحی ساده؛ نانوکاتالیست MnFe₂O₄؛ مایعات یونی؛ الکترولیت سبز؛ ظرفیت دشارژ بالا.