Electrochemical Properties of Lithium Air Secondary Batteries Incorporating Manganese Salen Complex as Soluble Catalyst for Nonaqueous Electrolyte Solutions

Shuhei SAKAMOTO,* Hironobu MINOWA, Masaya NOHARA, Mikayo IWATA, Masahiko HAYASHI, and Takeshi KOMATSU

NTT Device Technology Laboratories, NTT Corporation, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, Japan
* Corresponding author: hironobu.minowa.hg@hco.ntt.co.jp

ABSTRACT
Manganese-containing salen-type complexes of (R,R)-(−)-(−)-N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride (MnSl) were examined as a novel soluble catalyst in nonaqueous electrolyte solutions for lithium air secondary batteries (LABs). The LAB cells with MnSl exhibited a larger first discharge capacity and better cycle performance (893 mAh g\(^{-1}\), 738 mAh g\(^{-1}\) up to 10 cycles) than those without MnSl. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) conducted during the discharge/charge cycle showed deposition and decomposition of the discharge product, Li\(_2\)O\(_2\), on the surface of the air electrode. Cyclic voltammetry results suggested that MnSl promotes the oxygen reduction reaction and oxygen evolution reaction because of its high reactivity with O\(_2\).

Keywords: Lithium Air Secondary Battery, Manganese-containing Salen-type Complexes, Soluble Catalyst, Nonaqueous Electrolyte

1. Introduction
Lithium air secondary batteries (LABs) have attracted significant attention as possible power sources for electric vehicles, portable electronics, and stationary storage because they have the highest theoretical energy density among secondary batteries.\(^1,2\) Since oxygen supplied from the air is the active material of the air electrode, a theoretical specific energy density of 3505 Wh kg\(^{-1}\) has been calculated from the amount of Li\(_2\)O\(_2\) deposited in the discharge reaction, and the open circuit voltage (OCV) is 2.96 V.\(^1,2\) The discharge reaction in LABs using a nonaqueous electrolyte solution is an oxygen reduction reaction (ORR), in which lithium ions react with oxygen in the air such that Li\(_2\)O\(_2\) is deposited on the surface of the air electrode. The charge reaction is an oxygen evolution reaction (OER) that electrochemically decomposes Li\(_2\)O\(_2\). One of the major problems with LABs is the large discharging/charging overvoltage caused by the discharge voltage of about 2.6 V and charge voltage of about 4.5 V, which leads to poor cycle performance.\(^2\)

To decrease the large over-potential, various solid catalysts have been loaded into the air electrodes, including metal oxide (α-MnO\(_2\), CoMn\(_2\)O\(_4\), MnO\(_2\) nanoflakes, CoO\(_x\), and RuO\(_2\))\(^3,4\), a composite of metal and oxide (Pd/MnO\(_2\))\(^5\) and metal alloy (Pt\(_{100}\)-Ru\(_{2}\) and PtAu nanoparticles)\(^6,11\). The problem is that the solid catalysts are gradually deactivated because the discharge product, Li\(_2\)O\(_2\), accumulates on the surfaces of the catalysts in the air electrodes as a result of imperfect decomposition during the charge reaction after a large number of cycles.\(^1,15\) By dissolving the catalysts for the ORR and OER in nonaqueous electrolyte solutions, it is expected that they will act stably during discharge/charge cycles and not be deactivated by the undecomposed Li\(_2\)O\(_2\). Such soluble catalysts would overcome the above issues associated with solid catalysts. In recent years, 2,2,6,6-tetramethylpipеридин-1-й (TEMPO)\(^13\) and tris[4-(diethylamino)phenyl]amine (TDPA)\(^14\) have been reported as redox mediators, which have a function similar to that of a soluble catalyst. In addition, 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ)\(^15\) and iron pthalocyanine (FePc)\(^16\) have been reported as soluble catalysts. Both soluble catalysts and redox mediators improve cycle performance. The redox mediators reduce the over-potential for the ORR by reducing the potential below the open circuit voltage (OCV) of 2.96 V and for the OER by having an oxidation potential above OCV without an Ar or O\(_2\) atmosphere causing a change in current density.\(^13,14\) On the other hand, soluble catalysts enhance electrochemical activities for ORR and OER because of their capability of adsorbing oxygen or Li ions.\(^15,16\) The difference between redox mediators and soluble catalysts can be confirmed by making cyclic voltammetry (CV) measurements. For example, a LAB cell with TEMPO shows a lower charging voltage than one without it. The charging voltage has been reported to be predominantly determined by the redox potential of TEMPO 3.7 V versus Li/Li\(^+\). The reduction and oxidation peak currents of TEMPO have almost the same value, about 1.2 mA cm\(^{-2}\) in an Ar and O\(_2\) atmosphere.\(^13\) On the other hand, a LAB cell with DBBQ has a larger discharge capacity and higher discharge voltage than one without it; this leads to a larger reduction peak current of about 4.5 mA cm\(^{-2}\) in an O\(_2\) atmosphere than the current of about 2.0 mA cm\(^{-2}\) in an Ar atmosphere.\(^15\) Thus, these two types of catalyst-like additive—redox mediators and soluble catalysts—show potential for improving the cycle performance by reducing the over-potentials. However, as little is known about soluble catalysts, we need to develop additives with relatively simple and highly flexible structures.

Here, we investigated (R,R)-(−)-(−)-N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride (MnSl) for its electrochemical activity in deposition and decomposition of Li\(_2\)O\(_2\). The molecular structure of MnSl is shown in Fig. 1. MnSl is a Schiff base complex that is easily synthesized and whose structure can be easily manipulated around the active metal sites.\(^15\) It has been reported that some Schiff base complexes are capable of reversibly adsorbing and releasing oxygen at the central metals of the...
complexes and thus promote electrocatalytic activity for oxygen reduction reaction (ORR) in aqueous HClO₄ solution. Moreover, regarding the catalytic rate constant of the ORR estimated by chronocoulometry, solid-phase MnSl in/on the MCM-41 type silica spheres loaded onto a glassy carbon electrode has been reported to have a higher catalytic rate constant among the Schiff base complexes and some phthalocyanines (PCs) reported. Several studies have reported that catalysts included manganese exhibiting promise electrocatalytic performances for OER and ORR among transition metals. Therefore, we use MnSl as a target catalyst. Moreover, it has been reported that MnSl in nonaqueous electrolyte DMSO exhibits the reduction and oxidation processes. Phthalocyanines changing its valence of central metals have been reported to improve LAB performances by adsorbing and releasing oxygen. In brief, similar to phthalocyanines, MnSl as a soluble catalyst can be expected to improve LAB performances. Since the molecular weight of MnSl is smaller than phthalocyanines, it has high material selectivity. It can be also expected to be developed in future.

In this study, we investigated the electrochemical properties of LABs using MnSl as a soluble catalyst for nonaqueous electrolyte solutions with the aim of improving the discharge/charge performance. Electrochemical measurements were carried out to investigate whether the deposition and decomposition of the discharge product, Li₂O₂, proceeded in these LABs.

2. Experimental

2.1 Preparation of electrolyte solution with MnSl

MnSl powder was obtained from Sigma-Aldrich Co. LLC. It was vacuum-dried at 100°C for 12 h. As a representative electrolyte solution for LABs, 1 mol L⁻¹ LiTFSA/TEGDME was used for its resistance to superoxide attack. The electrolyte solution was prepared by mixing 0.005 wt% of MnSl in 1 mol L⁻¹ LiTFSA/TEGDME (tetracylme, Tomiyama Pure Chemical Industries Ltd.). Since MnSl is difficult to dissolve, it was dissolved by ultrasonic agitation for 2 h. Even when left for a week after preparation of the electrolyte solution, precipitation was not confirmed and the clear state was maintained.

2.2 Electrochemical characterization of electrolyte solution with MnSl

Electrochemical stabilities of MnSl in the electrolyte solutions were investigated by linear sweep voltammetry (LSV) measurements using a potentiostat/galvanostat (VMP3, BioLogic Science Instruments). A working electrode and a counter electrode were platinum disks (thickness: 0.5 mm) (The Nilaco Co.), and a reference electrode was a lithium fragment (Honjo Metal Co., Ltd.). Experimental cells were assembled using commercial three-electrode cells (ECC-Air, EL-Cell GmbH). The measurement conditions were a scan rate of 100 mV s⁻¹ and the voltage range of OCV to −1.0 V and OCV to 7.0 V at room temperature in an Ar-filled glovebox (UNIlab Plus Glove Box Workstation, MBRAUN Inc.). Conductivities of 1 mol L⁻¹ LiTFSA/TEGDME with/without 0.005 wt% MnSl were measured with two electrode cells using an LCR meter (ZM2371, NF Co.). Platinum black was used as a counter electrode and a working electrode. The measurement condition was the frequency of 10 kHz at 25°C under dry air atmosphere.

The electrocatalytic activity of 1 mol L⁻¹ LiTFSA/TEGDME with/without 0.005 wt% MnSl was investigated by making CV measurements with the three-electrode cells using the VMP3. The compositions of the cells were the same as in the LSV tests. The measurements were conducted at a scan rate of 100 mV s⁻¹ over a voltage range from 2.0 to 4.4 V at room temperature in the Ar-filled glovebox or an O₂-filled desiccator.

2.3 Assembly of LAB cells and performance tests

An air electrode with a diameter of 17 mm was prepared by coating carbon paper (TGP-H-120, Toray Industries Inc.) with a slurry of Ketjenblack EC-600JD (KB, 80 wt%) and polyvinilidene difluoride (PVdF, 20 wt%) in N-methyl-2-pyrrolidone solvent (Kishida Chemical Co., Ltd.) and drying it at 100°C for 24 h. Li foil (thickness: 0.6 mm) (Honjo Metal Co., Ltd.) was used as the negative electrode. A glass fiber sheet (thickness: 1.55 mm, diameter: 18 mm) (EL-Cell GmbH) soaked in an electrolyte solution was used as a separator. The experimental LAB cells were assembled using commercial cells (ECC-Air, EL-Cell GmbH). All of the LAB cell assembly processes were conducted in a dry air atmosphere with a dew point of less than −60°C. The galvanostatic discharge/charge performance tests were conducted on the VMP3 at a current density of 200 mA/g. The measurement conditions were a cutoff voltage from 2.0 to 4.4 V at room temperature in a dry air atmosphere. The current density and discharge/charge capacity were normalized by the mass of KB and PVdF, which are related to the reaction in the air electrode.

2.4 Characterization of discharged/charged air electrodes

The discharged/charged air electrodes were rinsed with dimethyl carbonate (DMC) (Tomiyama Pure Chemical Industries Ltd.) and vacuum-dried for 30 min. The obtained electrodes were analyzed by the following methods.

The deposition and decomposition of the discharge products at the electrolyte/air electrode interface were examined by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, JASCO Corp.). Li₂O₂ powder (Sigma-Aldrich Co. LLC.) was also examined as a reference. The morphologies and the elemental mappings of the air electrode surfaces were observed with a field-emission scanning electron microscope (FE-SEM) (ULTRA55, Carl Zeiss AG) with an energy dispersive X-ray spectrometer (EDS, BRUKER, QUANTAX).

3. Results and Discussion

3.1 Electrochemical characterization of electrolyte solution with MnSl

To investigate the electrochemical stability of MnSl in an electrolyte solution of 1 mol L⁻¹ LiTFSA/TEGDME, the potential windows of the electrolyte solutions with/without MnSl were examined by making LSV measurements using the three-electrode cells in an Ar atmosphere (Fig. 2). The potentials for the working electrode were swept from OCV to −1.0 V versus the reference electrode (Li/Li⁺) and from OCV to 7.0 V versus Li/Li⁺ at a scan rate of 100 mV s⁻¹. Large currents due to decomposition of the electrolytes occurred around 0 V and 5.0 V. Both the electrolytes exhibited stable potentials in a range from 0 to 5.0 V. MnSl in the electrolyte also exhibited stable potentials in that range. The conductivity measurements indicated that the electrolytes with/without MnSl had almost the same conductivity (2.65 × 10⁻³).
S cm$^{-1}$). These results indicate that MnSl was stable and did not decompose in the electrolyte solution from 0 to 5.0 V and had no effect on the conductivity of the electrolyte solution.

To investigate the electrocatalytic activity of MnSl in the electrolyte solutions related to the ORR and OER, CV measurements were conducted on electrolyte solutions with/without MnSl between 2.0 and 4.4 V at a constant scan rate of 100 mV s$^{-1}$ (Fig. 3). In the Ar atmosphere, the CV curves for the cases with or without MnSl did not show any significant reduction or oxidation peaks (Fig. 3a). In the absence of MnSl, the CV curve measured in the Ar atmosphere resembled the one measured in the O$_2$ atmosphere, except that the curve measured in the O$_2$ atmosphere had a minute peak corresponding to the OER at about 3.3 V (Fig. 3a and Fig. 3b). These results indicate that there were no reduction/oxidation peaks corresponding to the redox of MnSl in the voltage range. The minute peak of the OER process appearing only in the curve measured in the O$_2$ atmosphere indicates that the 1 mol l$^{-1}$ Li$_2$TFSAl/TEGDME electrolyte solution had low activity with O$_2$. In the O$_2$ atmosphere, the reduction/oxidation current densities increased over the whole potential range in the presence of MnSl (Fig. 3b). Since there was no peak corresponding to redox of MnSl in the Ar atmosphere, the current density increased in the presence of MnSl as a result of its interaction with O$_2$. This behavior led to the higher activities for the ORR and OER. Moreover, the onset potential of the ORR shifted significantly in the positive direction and the peak current of the OER rose in the presence of MnSl. This behavior indicates that the discharging and charging became easier. Overall, these results suggest that MnSl is a soluble catalyst rather than a redox mediator.

### 3.2 First discharge/charge properties of LAB cells

Figure 4 shows the first discharge/charge curves of the LAB cells with/without MnSl at a current density of 200 mA g$^{-1}$. The first discharge capacities were 363 and 893 mAh g$^{-1}$, respectively. In the discharging process, the cell with MnSl maintained a higher voltage than the cell without it to the end of the discharging process. The high discharging voltage is related to the shift in the onset potential of ORR in the CV results, as shown in Fig. 3b. In the charging process, the cell with MnSl showed a larger capacity of 676 mAh g$^{-1}$ and lower voltage at the beginning of the process in comparison with the cell without it. The curve for the cell with MnSl has a sloped curve at around 4.0 V, showing that it maintained a lower charging voltage than the cell without MnSl. It seems that the 4.0 V plateau is related to the peak potential of the oxidation peak that appeared in the cell with MnSl (Fig. 3b). The high ORR/OER activities of MnSl point to it being a soluble catalyst.

### 3.3 Characterization of discharged/charged air electrodes

To investigate the morphologies of the discharge products, we obtained SEM images of the air electrodes in the LAB cells with/without MnSl before the first discharge, after first the discharge, and after the first charge (Fig. 5a). Whereas the electrode surface before discharge was free of any discharge products, after the first discharge fine sub-micrometer discharge products covered the surfaces of the carbon particles in the electrodes with/without MnSl. The discharge products in the presence of MnSl were deposited and decomposed more uniformly and were larger in size than in the absence of MnSl. Most of the carbon particles that were covered by the discharge products had a diameter of approximately 100 nm. After charging, the discharge products must have decomposed from the surfaces of the electrodes, because they became smaller than those after the discharge. We also obtained EDS mappings of the air...
electrodes after discharge showing the distribution of C and O (Fig. 5b). The EDS mappings were acquired in a wider range than the SEM images. The distributions of C and O are almost overlapping in the electrodes with/without MnSl. The EDS analyses indicate that the discharge products related to O cover the electrode surface of C. Moreover, the signal of O in the electrode with MnSl is stronger than that in the electrode without MnSl. The analyses also indicate that the amount of discharge products in the electrode with MnSl are larger than that in the electrode without MnSl. These behaviors are reflected in the results of the first discharge/charge curves and SEM images (Fig. 4 and 5). On the other hand, since the discharge products were not completely decomposed after charging, the charge capacity was smaller than the discharge capacity (Fig. 5).

To identify the discharge products, the air electrodes with/without MnSl before the first discharge, after the first discharge, and after the first charge were examined by ATR-FTIR (Fig. 6). The ATR-FTIR absorbance peaks at around 500 cm$^{-1}$ in the discharged electrodes can be assigned to Li$_2$O$_2$ reference powder. No other peaks from other byproducts are visible. The position of the peak is similar to that in a previous study. The peak appeared after the discharge and disappeared after the charge. These results suggest

**Figure 4.** First discharge/charge curves of LAB cells using 1 mol/l LiTFSA/TEGDME with/without MnSl at a constant current density of 200 mA g$^{-1}$ under dry air atmosphere.

**Figure 5.** SEM images of the air electrode as prepared, after discharge, and after charge (a) and EDS mappings of C and O of that after discharge (b) using 1 mol l$^{-1}$ LiTFSA/TEGDME with/without MnSl.

**Figure 6.** FTIR spectra of the air electrodes using 1 mol l$^{-1}$ LiTFSA/TEGDME (a) with/(b) without MnSl.

Electrochemistry, 87(6), 365–369 (2019)
deposition and decomposition of Li$_2$O$_2$ occurred during the discharge/charge process. On the other hand, there is no peak ascribable to Li$_2$O, despite that one was reported from 450 to 500 cm$^{-1}$. The absorbance of Li$_2$O$_2$ is more clearly exhibited in the presence of MnSl than in the absence of it. This result suggests that MnSl increased the amount of deposited Li$_2$O$_2$. These results correspond to the SEM images showing more discharge products in the presence of MnSl than in the absence of it. The deposition and decomposition reactions of Li$_2$O$_2$ thus proceeded in the LAB cell with MnSl.

### 3.4 Cycle performance of LAB cells

Figure 7 shows the cycle performance of the LAB cells with/without MnSl. The cell with MnSl had larger discharge capacities up to 15 cycles than the one without it. In the cell with MnSl, the discharge capacities were increased up to 3 cycles, and the maximum capacity was 1481 mAh g$^{-1}$. The electrolyte with MnSl may have gradually penetrated the air electrode as the cycle proceeded because of its high viscosity. The discharge capacities remained relatively stable from the 3rd to 6th cycle. It gradually degraded after the sixth cycle. The results for the 3rd to 6th cycle suggest that MnSl exhibits inherent electrocatalytic activity as a result of the electrolyte sufficiently penetrating the electrode. The electrolyte solution decomposed after the 6th cycle, as a result of exposing it to a high voltage of 4.0 V or more in each charging process (Fig. 4). Because of the decomposition, the discharge and charge overvoltage increased and the capacity gradually decreased. The LAB cells with MnSl exhibited better cycle performance (773 mAh g$^{-1}$) than those without MnSl (64 mAh g$^{-1}$) for up to 10 cycles. MnSl thus has the potential to promote deposition and decomposition of Li$_2$O$_2$ through its electrocatalytic activity.

Since the reaction mechanism of MnSl in the electrolyte solution is still unclear, further study is needed. In the future, investigating the interaction of MnSl with active materials of Li$^+$ and O$_2$ by in situ analysis such as XRD analysis and TEM observation will help to understand the mechanism.

### 4. Conclusion

The suitability of MnSl as an additive for nonaqueous electrolyte solutions of LABs was investigated. The conductivity of MnSl in an electrolyte solution was stable between 0 and 5.0 V versus Li/Li$^+$. The measured CV curves indicated that MnSl enhanced the activities for ORR and OER in an O$_2$ atmosphere and acted as a soluble catalyst instead of a redox mediator. The cell with MnSl had a large discharge capacity (893 mAh g$^{-1}$) as well as a higher discharging voltage and lower charging voltage than the one without MnSl. An ATR-FTIR analysis of the deposition and decomposition of discharge product, Li$_2$O$_2$, on the air electrode surfaces during the discharge/charge process indicated that MnSl is an efficient soluble catalyst for nonaqueous electrolyte solutions for LABs which provides improved discharge capacity, discharge voltage, charge voltage, and cycle performance.

### References