

## Fabrication and Conductivity Characteristics of Some $\text{Li}_2\text{O}_2$ -LiX Electrolytes

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The fabrication and characteristics of lithium halides have been studied by various investigators.<sup>1-5</sup> Lithium halides have received much attention as a solid electrolyte material.

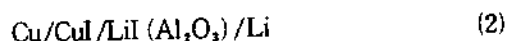
The formation of crystal defects in lithium halides by addition of minute quantities of higher valent cations has shown an increase of ionic conductivities.<sup>1,3</sup>

Lithium iodide of lithium halides itself was only a moderate conductor of lithium ions. Its room temperature conductivity and open-circuit voltage (ocv) of the cell (equation 1)



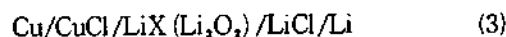
were about  $10^{-7}$  (ohm cm)<sup>-1</sup> and 2.1 V, respectively. In 1973 Liang<sup>4</sup> reported that the addition of finely divided alumina to LiI produced a significant of lithium ion conductivity. The best conductivity, about  $10^{-5}$  (ohm cm)<sup>-1</sup> at 25 °C, occurred at approximately 45 mole % of  $\text{Al}_2\text{O}_3$ , an improvement of about two orders of magnitude over pure LiI.

The ocv of Liang's cell (equation 2)



was about 2.1 V at 25 °C.

The purpose of this paper is to study how to increase the ocv and the current density (or characteristics) of solid state batteries (equation 3)



by use of high pressure and *o*-ring shaped parafilm. In order to do this, the internal resistance and the dendritic effect had to be minimized at the electrolyte/electrode interfaces.

Prepared material, anhydrous LiX ( $X^- = \text{Cl}^-, \text{BF}_4^-$  and  $\text{AsF}_6^-$ ) and  $\text{Li}_2\text{O}_2$  to make mixed electrolytes were used without purification in a He-Ar box.

By compression in a hand-actuated laboratory press, pellet samples were prepared by pressing the mixed powder in a 1.5 cm diameter steel die. Under a pressure of 6877.6 atm. with electrodes incorporated on both sides of the pellet.

The geometric area and thickness of the pellet was measured by a micrometer. The resistance of the cell was measured by using an impedance bridge at 1 KHz. The steady-state cell current was measured by the potential drop across a standard resistor in series with the cell. The cell potential and the potential at the standard resistor were measured by the H-P Digital Electrometer.

Experimental details are described elsewhere.<sup>1,4</sup> In 1969 Liang<sup>5</sup> used the vacuum deposition method to make a solid state battery (equation 1). Its ocv was about 2.1 V and at this time the film thickness of the used electrolyte LiI was smaller than  $5 \times 10^{-6}$  cm. The conductivity of the thin-film cell was expected to be  $10^{-7}$  (ohm cm)<sup>-1</sup> at 25 °C. But lithium

**Table 1.** OCV and Current Density of Cu/CuCl/LiX ( $\text{Li}_2\text{O}_2$ )/LiCl/Li with/without  $\text{Li}_2\text{O}_2$  or Parafilm at room temperature and 6877.6 atm

OCV (V)	Current Density ( $\mu\text{A}/\text{cm}^2$ )	Thickness (cm)	CuCl (g)	$\text{Li}_2\text{O}_2$ (g)	LiX (g)	Parafilm	Remarks ( $X^-$ )
2.85*			0.8		1.2		$\text{Cl}^-$
2.87*			0.8	0.8	0.8		$\text{Cl}^-$
3.05	0.5	0.41	0.8		0.8		$\text{BF}_4^-$
2.83	0.07	0.41	0.8		0.8		$\text{Cl}^-$
2.94	0.002		0.8		0.8	$\text{P}_2$	$\text{Cl}^-$
3.2	6	0.20	0.26	0.14	0.14	$\text{P}_1, \text{P}_2\text{P}_2$	$\text{Cl}^-$
2.7	6	0.20	0.26	0.14	0.14	$\text{P}_1, \text{P}_2\text{P}_2$	$\text{AsF}_6^-$
3.45	77	0.09	0.26	0.14	0.14	$\text{P}_1, \text{P}_2$	$\text{BF}_4^-$

\*; 25 °C,  $\text{P}_1$ : used single *o*-ring parafilm at CuCl/LiX( $\text{Li}_2\text{O}_2$ ) interface,  $\text{P}_2$ : used single *o*-ring parafilm at LiX( $\text{Li}_2\text{O}_2$ )/LiCl interface,  $\text{P}_2\text{P}_2$ : used double *o*-ring parafilm at LiX( $\text{Li}_2\text{O}_2$ )/LiCl interface.

iodide containing 33-45 mole %  $\text{Al}_2\text{O}_3$  exhibited conductivity in the order of  $10^{-6}$  (ohm cm)<sup>-1</sup> at 25 °C.

In this study, when only LiX ( $X^- = \text{Cl}^-$  and  $\text{BF}_4^-$ ) was pressed under a pressure of 6877.6 atm, its ocv and current density has shown values from 2.83 to 3.05 V and 0.002 to  $0.07 \mu\text{A}/\text{cm}^2$ .

Nevertheless, when  $\text{Li}_2\text{O}_2$  and LiX ( $X^- = \text{Cl}^-$ ,  $\text{BF}_4^-$  and  $\text{AsF}_6^-$ ) used under the same pressure were composed of the same weight percentage (shown in Table 1), its ocv and current density within the observed ranges is from 2.7 to 3.45 V and  $6-77 \mu\text{A}/\text{cm}^2$ , respectively. By using 50 mole %  $\text{Li}_2\text{O}_2$  for LiX, these mixed electrolytes might be converted as porous material<sup>6</sup>, and it is suggested that through this process, the movement of  $\text{Li}^+$  ions will be easier because, according to Liang<sup>1,2</sup> and others<sup>6,7</sup>, the conduction mechanism of the lithium chloride-lithium peroxide is identical with that of lithium chloride and that lithium ion vacancies are the principal mobile species.

At low discharge voltage ( $E^\circ = -1.41\text{V}$ ) the  $\text{Li}_2\text{O}_2$  reacts sufficiently with the activated Li metal, and in the next step, after activated copper metal exists between the CuCl electrode and the mixed electrolyte interfaces, several reactions occur. In the Li-CuO galvanic cell, Novák<sup>8,9</sup> reported these reaction mechanisms, but in the Li-CuCl solid state battery, these reaction mechanisms will be reported in detail later.<sup>10</sup>

It was assumed that copper ions, which exist unnaturally because of a defect in the structure of the *p*-type semiconductor CuCl at CuCl/LiX( $\text{Li}_2\text{O}_2$ ) interface will react easily with  $\text{Li}_2\text{O}_2$  and others.

Its ocv increases up to 2.32 V because  $\text{Li}^+$  ions occur after

the reaction of  $\text{Li}_2\text{O}$  and  $\text{Cu}_2\text{O}$  etc. In the last step after the reaction of  $\text{LiX}$  and  $\text{Cu}$  and so on, its ocv occurs up to 3.07 V. So, in order to prepare the cell which ocv has to obtain a higher value under a pressure condition, make sure to connect all electrode/electrolyte interfaces (Table 1) well.

And also it's reasonable to believe that in increase of conductivity is caused by a remarkable decrease of the internal resistance by high pressure and heterogeneity by the presence of heterogeneous mixture at  $\text{CuCl/LiCl}$  ( $\text{Li}_2\text{O}_2$ ) interface.

In consequence of our studies, the high voltage and the conductivity of solid ionic electrolytes, consisting of  $\text{LiX}$  ( $\text{X}^- = \text{Cl}^-$ ,  $\text{BF}_4^-$  and  $\text{AsF}_6^-$ ) and lithium peroxide which will probably be similar to the  $\text{Al}_2\text{O}_3$  structure under 6877.6 atm, can be substantially improved up to 2.7 to 3.45 V and about  $10^{-6}$  to  $10^{-5}$  ( $\text{ohm cm}$ ) $^{-1}$  at room temperature.

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## Novel Reaction of N-Bromoamides with Superoxide Anion Radical: Formation of N,N'-Diacylhydrazines

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Recently, intensive studies have been focused on the reaction of superoxide anion with heteroatom compounds such as nitrogen<sup>1</sup> and sulfur compounds<sup>2</sup>. N-Bromoamide was first reacted with potassium superoxide in acetonitrile expecting to obtain isocyanate by Hofmann rearrangement<sup>3</sup>. In this reaction, however, any formation of isocyanate could not be observed, but N,N'-diacylhydrazine was obtained as the main product. Now, we report this new reaction and a possible reaction mechanism.

In a typical run, a solution of N-bromobenzamide<sup>4</sup> (200 mg, 1 mmol; dry acetonitrile: 2 ml) was added to the suspension of potassium superoxide (86 mg, 1.2 mmol; dry acetonitrile: 3 ml) at  $-35^\circ\text{C}$  under argon atmosphere. The reaction mixture was stirred for 10 h at  $-20^\circ\text{C}$  in a refrigerator. Ethyl ether (*ca.* 3 ml) was added to the reaction mixture to precipitate, and the resulting mixture was filtered and washed with water to afford white crystals (96.8 mg, 80%). The crystals were identified to be N,N'-dibenzoylhydrazine by <sup>1</sup>H NMR, mass spectrum ( $m/e = 240$  ( $\text{M}^+$ )), and mp ( $238 \sim 239^\circ\text{C}$ , lit<sup>5</sup>  $239.5 \sim 240.5^\circ\text{C}$ ). The results obtained were summarized in Table 1.

The superoxide anion has been known to act not only as a base but also as a good oxidant by transferring one electron<sup>6</sup>. If the superoxide anion attacks N-bromoamide as a base, the N-bromoamide will be converted to the corresponding isocyanate by Hofmann rearrangement. The resulting products in Table 1, however, showed that no rearrangement occur-

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**Table 1.** Products from the Reaction of N-Bromoamide with Potassium Superoxide

$$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{Br} + \text{KO}_2 \xrightarrow{\text{CH}_3\text{CN}} (\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH})_2 + \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 + \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$$

Entry	R	KO <sub>2</sub> /1	2 (%) <sup>a</sup>	3 (%) <sup>a</sup>	4 (%) <sup>a</sup>
1	C <sub>6</sub> H <sub>5</sub>	0.6	35	—	—
2	"	1.2	80	—	—
3	"	1.5	79	—	traceable
4	"	2.0	60	—	23
5	"	4.0	traceable	—	85
6	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	1.2	83	—	—
7	CH <sub>3</sub>	1.2	56	32	—

\*: Isolated Yields.

red. Since the superoxide anion is known to transfer one electron easily, it may attack N-bromoamide 1 to afford amide radical 5 and molecular oxygen<sup>7</sup>. The unstable amide radical 5 may be coupled to N,N'-diacylhydrazine 2 or converted to the amide 3 by abstraction of hydrogen atom.

When the excess amount of superoxide anion existed, the amide radical 5 might be converted into N-peroxyamide anion intermediate 6 by the coupling with superoxide anion,