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Short Coumminication

The Dependence of the Electrochemical Performance of Ambient Li-SO_2 Primary Cells on the Electrolyte Solvent

Tae Hyeon Yang, Yongju Jung[*]

Department of Chemical Engineering, Korea University of Technology and Education
(KOREATECH), Cheonan 330-780, Korea
[*]E-mail: yjung@koreatech.ac.kr

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The effect of the electrolyte solvent on the electrochemical performance of ambient Li-SO_2 primary cells was extensively investigated using four organic solvents: acetonitrile (AcN), dimethoxyethane (DME), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The cells with DME, DMF or DMSO electrolytes delivered much higher discharge capacities (> 800 mAh/g), compared to those with a conventional AcN electrolyte. The DME electrolyte showed outstanding performance in terms of discharge capacity, rate property and energy density. In particular, the energy density of the test cells with a DME electrolyte was approximately 3.4-fold more than that with an AcN electrolyte when electrolyte solutions were saturated with SO_2.

Keywords: Li-SO_2 primary cells, Organic solvent, Acetonitrile, Dimethoxyethane

1. INTRODUCTION

Lithium-sulfur dioxide (Li-SO_2) primary batteries are a high-energy density lithium battery system with many advantages of excellent shelf life, high cell voltage, flat discharge profile, and wide operating temperature range[1-5]. During discharge, sulfur dioxide dissolved in an organic solution is reduced to dithionite ions ($S_2O_4^{2-}$) on the carbon cathode, and these ions react with lithium ions to generate $Li_2S_2O_4$, an insoluble salt. The superior storage properties of Li-SO_2 batteries, which are highly beneficial for military and industrial applications, are associated with the formation of a stable protection layer on the lithium anode surface through the chemical reaction of lithium and SO_2[1,3]. The internal cell pressure of Li-SO_2 batteries with a SO_2–containing acetonitrile (AcN) electrolyte is 3~4 atm in the undischarged state at room temperature[5-7]. This feature may cause serious safety problems under thermal and electrical abuse conditions (e.g., short circuit and overheating). For pressure relief and prevention of cell rupture, a safety vent is typically placed at the bottom of the cell.

Most studies have focused on the electrochemical properties of Li-SO_2 primary cells with an AcN electrolyte except for an ionic liquid electrolyte that is expected to greatly improve the safety of Li-SO_2 cells[8]. AcN-based electrolytes are used in Li/SO_2 primary batteries for military applications. But, AcN has a drawback of high vapor pressure, which can lead to increased internal cell pressure and potentially cell explosion[9-11].

In general, the physicochemical properties of an electrolyte solution (e.g., viscosity and vapor pressure of the electrolyte, solubility and solvation structure of SO_2) may be affected by an organic solvent. Nevertheless, the influence of organic solvents on the electrochemical reduction of SO_2 has not yet been comprehensively studied. In this study, the electrochemical properties of Li-SO_2 cells are investigated in four organic electrolyte solutions to find a promising organic solvent capable of replacing the current AcN solvent.

2. EXPERIMENTAL SECTION

Four organic solvents (battery grade, PANAX ETEC, Korea), including acetonitrile (AcN), dimethoxyethane (DME), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), were examined as electrolyte solvents for Li-SO_2 cells. Lithium bis(trifluoromethanesulphonyl)imide (LiTFSI, 99.95%, Sigma-Aldrich) used as a supporting electrolyte was dried at 120 °C under vacuum for 12 h to remove moisture. High purity SO_2 gas (>99.99%, Alpha Gas, Korea) was used to prepare the catholyte solutions of the Li-SO_2 cells. The solubility of SO_2 in 1.0 L of organic solutions containing 1.0 M LiTFSI was measured at 1 atm pressure. For comparative study, catholyte solutions were prepared by dissolving 6.34 moles of SO_2 gas in 1.0 L of organic solutions at room temperature. Moreover, 1.0 L of 1 M LiTFSI/DME solution saturated with SO_2 was obtained by dissolving about 9.64 moles of SO_2 for improving the energy density of ambient Li-SO_2 cells.

A slurry with 90 wt% Ketjenblack (EC-600JD, AkzoNobel) and 10 wt% polytetrafluoroethylene (PTFE, Sigma-Aldrich) binder was coated on a nickel mesh and dried to fabricate a carbon cathode, which was cut into 16-mm discs and dried at 150 °C under vacuum for 12 h before cell assembly. The electrochemical characteristics of the prepared catholytes were examined in the 2016 coin cells that were composed of the carbon cathode, a lithium metal anode and a glass fiber separator (GC50, Advantec). In addition, a series of Li-SO_2 cells with different SO_2 loadings were prepared and compared in the two catholytes based on AcN and DME in order to study the effect of SO_2 loading on the cell performance.

The fabricated Li-SO_2 cells were discharged to 2.0 V at various constant current densities of 0.25 ~ 5.00 A/g. The morphologies of discharge products obtained at the end of discharge were examined using field-emission scanning electron microscopy (FESEM, JEOL JSM-7000F).

3. RESULTS AND DISCUSSION

The solubility of SO_2 at 1 atm pressure was very sensitive to the type of organic solvent (Table 1). DMF and DMSO showed much higher solubility (> 13.5 moles per 1.0 L solution with 1.0 M LITFSI) compared to that of AcN (6.34 moles). For proper comparison, four types of catholyte solutions were prepared by dissolving 6.34 moles of SO_2 in 1.0 L of organic solutions at 1 atm pressure. The discharge performance of the Li-SO_2 cells with a constant SO_2 loading was investigated for the four different catholytes. The electrochemical properties of SO_2 depended significantly on the type of organic solvents used, as shown in Fig. 1.

Table 1. Physicochemical properties of organic solvents and discharge capacities of the Li-SO_2 cells with different organic catholytes at the SO_2 loading of 8.5 mg/cm^2.

Solvent	Solubility of SO_2 (mol) [a]	Viscosity (cp) [b]	Discharge capacity (mAh/g) [c]	
			0.25 A/g	5.00 A/g
AcN	6.34	0.35	503	474
DME	9.64	0.47	1180	1087
DMF	13.7	0.92	1038	320
DMSO	19.5	1.99	802	294

[a] Measured in 1.0 L of solution with 1.0 M LiTFSI at 1 atm pressure.
[b] Viscosity of pure solvent at 20°C.
[c] Capacity per gram of carbon.

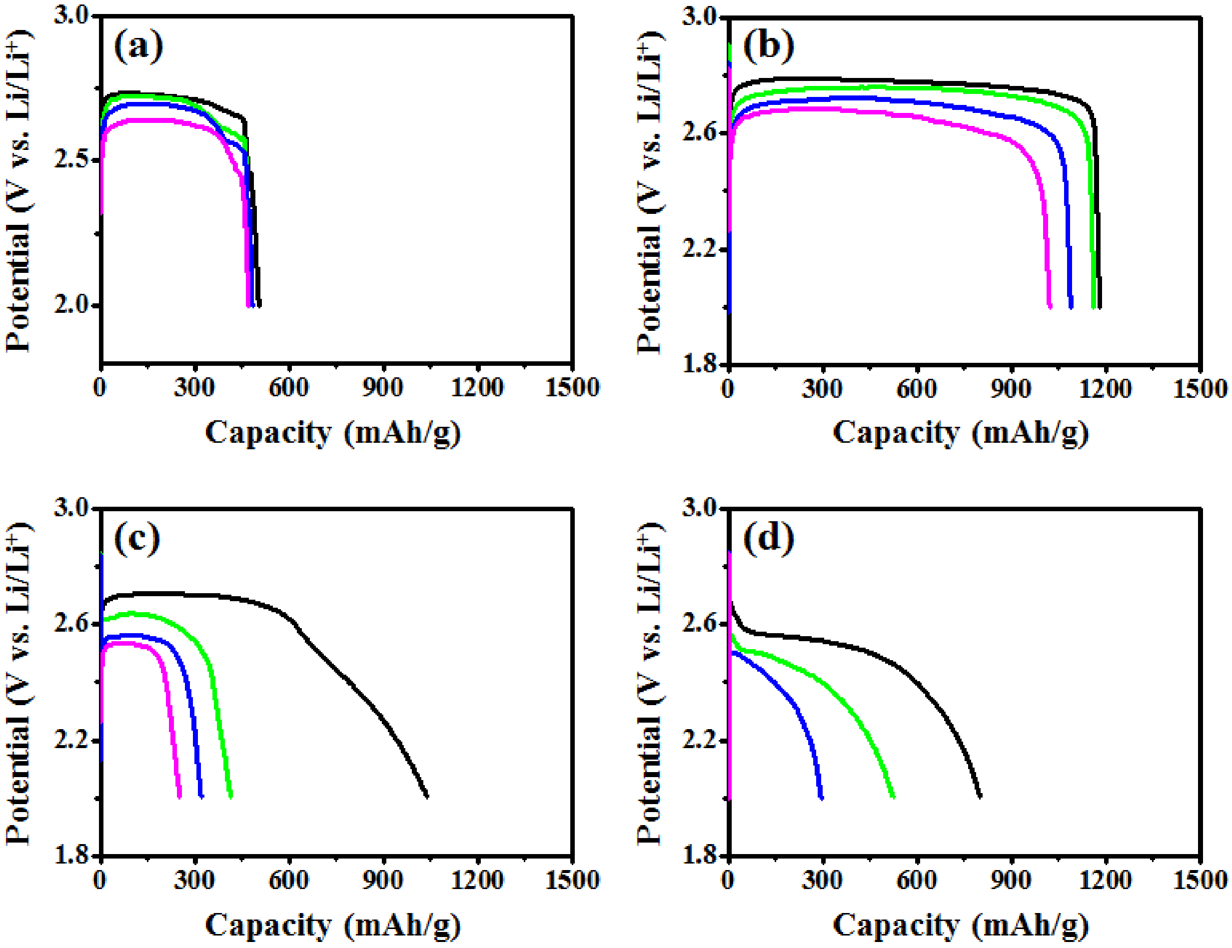

Figure 1. Discharge profiles of the Li-SO_2 primary cells with different catholytes: (a) AcN, (b) DME, (c) DMF, and (d) DMSO at various current densities of 0.25 A/g (—), 1.25 A/g (—), 2.50 A/g (—), and 5.00 A/g (—).

The cells with DME, DMF, and DMSO solutions exhibited much higher discharge capacities (> 800 mAh/g) at a low current density of 0.25 A/g than the cell with a conventional AcN solution. In particular, the discharge capacity of the DME catholyte was increased ~2.3-fold to 262 mAh/g-SO_2 with respect to the mass of SO_2, which corresponds to a consumption of approximately 62% of SO_2 when considering the theoretical capacity (420 mAh/g-SO_2) of the following electrode reaction: $2SO_2 + 2e^- \rightarrow SO_2^{2-}$[12]. The 112 mAh/g-$SO_2$ discharge capacity of the AcN catholyte indicated that only ~27% SO_2 was consumed. The insulating discharge product ($Li_2S_2O_4$) formed on the carbon surface may limit the charge transfer reaction of SO_2 molecules[2]. As a result, the discharge capacity may be directly affected by the physicochemical nature of discharge product accumulated on the electrode surface, which may be dependent on the type of solvents.

Figure 1 also shows the rate properties of the Li-SO_2 cells with the four different electrolyte solvents. The potential profiles and discharge capacities with increasing current density depended significantly on the solvents. The DMF and DMSO catholytes showed a substantial decrease in discharge capacity with increasing current density, which was tentatively attributed to the high viscosity of these solvents. However, the DME catholyte showed a high capacity (1021 mAh/g) at a high current density of 5.00 A/g that was more than double that (471 mAh/g) of the AcN catholyte. These results demonstrate DME's promising potential as a solvent for high performance Li-SO_2 primary cells.

Figure 2 shows the FESEM images for the carbon cathodes which were taken at the end of the discharge. In the catholytes containing DME, DMF or DMSO solvents, dense films were formed on the carbon cathodes due to the precipitation of the insoluble discharge products, $Li_2S_2O_4$. On the other hand, deposit layers with porous structure were found in the cell with an AcN solvent. This feature can be attributed to the difference in the amount of $Li_2S_2O_4$ generated upon discharge.

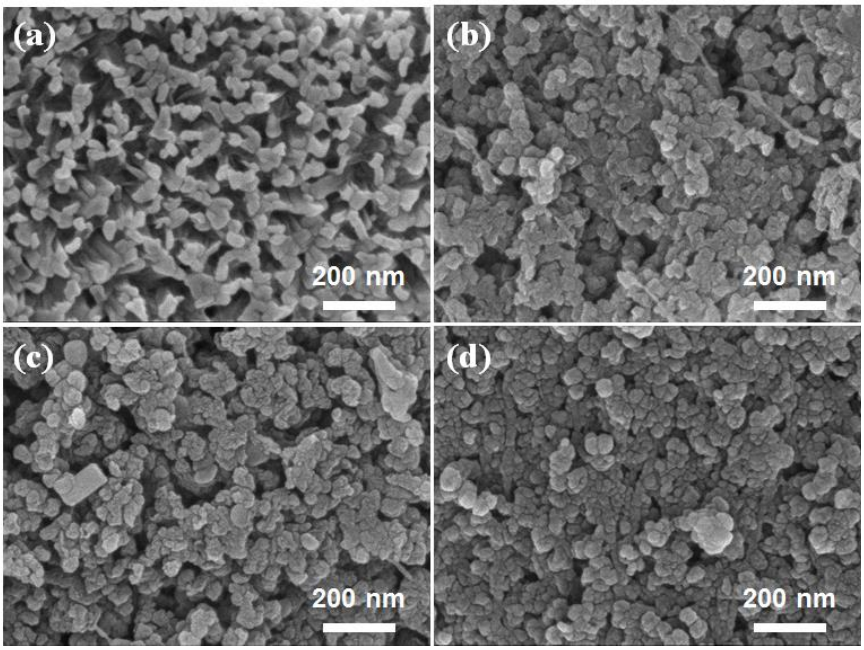

Figure 2. FE-SEM images taken at the end of discharge for the carbon cathodes with different catholytes.

Upon discharging, LiCl cubic crystals are produced on the surface of the carbon cathode in Li-SO_2 rechargeable cells with an inorganic electrolyte based on lithium tetrachloroaluminate ($LiAlCl_4$)[12-14], whereas $Li_2S_2O_4$ precipitates are accumulated on the cathode surface in Li-SO_2 primary cells containing an organic electrolyte solution[1-5]. It was reported that the discharge product, $Li_2S_2O_4$, affects the mass transport of an electrolyte solution, resulting in inhibiting further reduction of SO_2[2]. For this reason, it can be expected that the mass transport resistance would be much severer in DME, DMF and DMSO solvents than in AcN solvent. Very interestingly, however, the cell with an AcN solution showed the lowest discharge capacity, indicating that the discharging behavior of SO_2 in organic solutions may be governed by other factors such as the uniformity of deposit films and the chemical nature of SO_2 in a solution.

Figure 3a and 3b shows the effect of SO_2 loading on the electrochemical performance of Li-SO_2 cells containing AcN and DME solvents. When the SO_2 loading was increased from 8.5 to 13.0 mg/cm^2, an increase in the discharge capacities of the Li-SO_2 cells was more pronounced in DME. The energy density of the Li-SO_2 primary cells was calculated with respect to the total mass of the carbon cathode, the lithium metal anode and the catholyte. The cells with AcN or DME catholytes showed a similar trend in which the energy density gradually decreased with increasing SO_2 loading (Figure 3c). This is mainly due to the two following reasons. First, the increased discharge capacity can be offset by an increase in the weight of the catholyte, which is the most significant contributor to the total weight of the cells (Table 2). Second, the energy density of the Li-SO_2 cells is affected significantly by the rate of SO_2 consumption. In fact, the Li-SO_2 cells with DME exhibited a 10% decrease in the SO_2 consumption rate when the SO_2 loading was increased from 8.5 to 13.0 mg/cm^2 at a fixed carbon cathode.

Table 2. Areal capacities and energy densities of the Li-SO_2 primary batteries with organic catholytes at various SO_2 loadings

Solvent	SO_2 loading (mg/cm^2)	Carbon cathode (mg)	Catholyte (mg)	Lithium metal [a] (mg)	Areal capacity (mAh/cm^2)	Energy density [b] (Wh/kg)
DME	13.0	4.2	158.7	4.79	3.07	101.9
	11.5	4.2	140.4	4.31	2.76	102.6
	10.0	4.2	122.0	3.81	2.44	104.2
	8.5	4.2	103.8	3.48	2.23	110.9
AcN	13.0	4.2	150.5	1.80	1.15	40.2
	11.5	4.2	133.1	1.63	1.04	41.4
	10.0	4.2	115.7	1.52	0.97	43.4
	8.5	4.2	98.5	1.48	0.95	50.2

[a] Calculated with an N/P ratio of 3.0.
[b] Based on the total mass of the carbon cathode, the catholyte and the lithium metal anode.

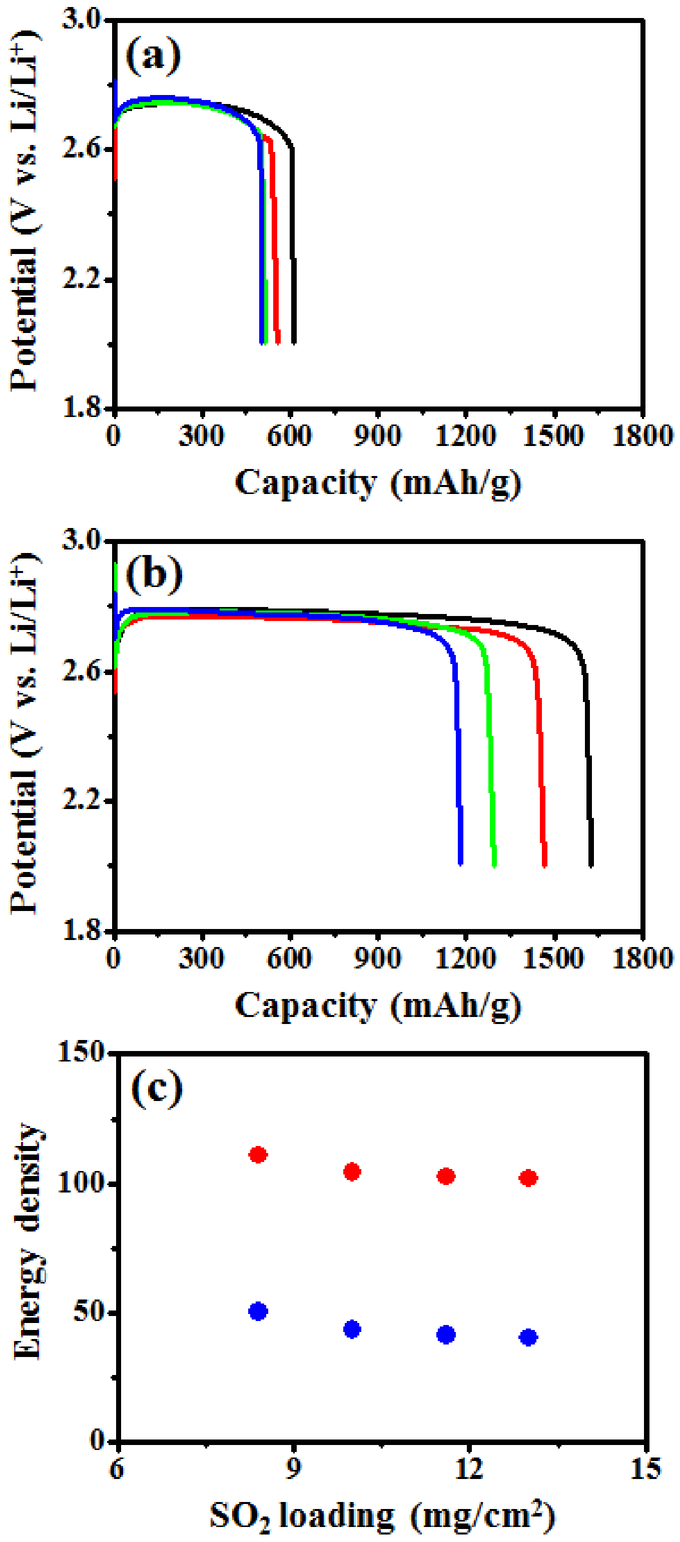

Figure 3. Discharge profiles of the Li-SO_2 cells containing (a) AcN and (b) DME catholytes with different SO_2 loadings of 8.5 mg/cm^2 (—), 10.0 mg/cm^2 (—), 11.5 mg/cm^2 (—), and 13.0 mg/cm^2 (—) at a current density of 0.25 A/g. (c) Effect of SO_2 loading on the energy density of the Li-SO_2 cells.

With the aim of improving the energy density of the Li-SO_2 cells, a SO_2-saturated DME catholyte was prepared and examined at various current densities. When the amount of dissolved SO_2 in 1.0 L of 1 M LiTFSI/DME solution was increased from 6.34 moles to 9.64 moles, the discharge capacity of the test cells was only increased by 10% at the same SO_2 loading of 11.5 mg/cm^2, as shown in Figure 4. However, there was a noticeable difference in the energy density, which was significantly improved from ~110 to ~140 Wh/kg. Compared with the SO_2-saturated AcN catholyte, the energy density of the SO_2-saturated DME catholyte was increased about 3.4-fold. At a high current density of 5.00 A/g, the test cells demonstrated an excellent capacity of 1365 mAh/g and extremely high capacity retention of ~88%. Based on the overall results, it is concluded that the use of DME-based catholytes in ambient Li-SO_2 cells will simply and efficiently improve performance in terms of energy density and safety.

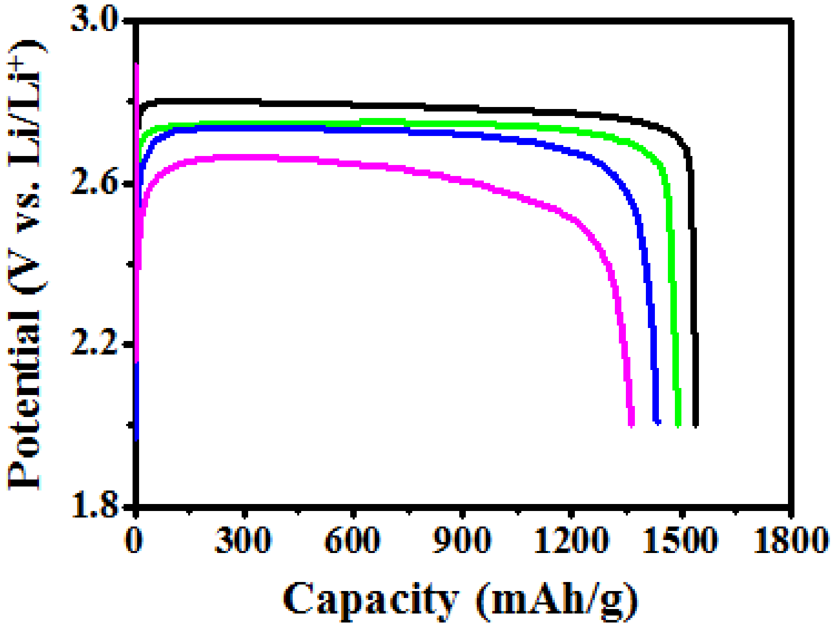

Figure 4. Discharge profiles of the Li-SO_2 primary cells with a SO_2-saturated DME catholyte at various current densities of 0.25 A/g (—), 1.25 A/g (—), 2.50 A/g (—), and 5.00 A/g (—).

4. CONCLUSION

A series of electrolyte solutions with four different organic solvents was prepared by dissolving 6.25 moles of SO_2 gas in 1 M LiTFSI solutions for use in ambient Li-SO_2 primary cells. The resulting electrochemical properties were evaluated at an internal cell pressure of 1 atm. The electrochemical performance of the test cells was critically dependent on the type of organic solvent. The discharge capacities of the test cells were significantly enhanced in DME, DMF, and DMSO electrolytes at a low current density of 0.25 A/g. The discharge capacities were drastically decreased in DMF and DMSO electrolytes when the current density was increased to 5.00 A/g, whereas the DME electrolytes exhibited excellent capacity retention. As the SO_2 loading was increased in the DME solution, the discharge capacity of the cells was improved, while the energy density of the cells was slightly decreased due to an increase in the mass of electrolyte, which is the most important factor in the total mass. However, Li-SO_2 cells with high energy density can be fabricated with a SO_2-saturated DME electrolyte. When these SO_2-saturated solutions were used as electrolytes at ambient pressure condition, the energy density of the test cells with DME solution was dramatically increased 3.4-fold compared to that with the AcN solution at the same SO_2 loading condition.

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