Density Measurement of Lithium Vapor in Multiphase AC Arc for Nanoparticle Production of Li-Mn Composite Oxide

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Abstract: An innovative measurement technique of number density of metal vapor in thermal plasmas was performed by optical spectroscopy with consideration of self-absorption of Li vapor. Self-absorption by Li atom at 671 nm in thermal plasmas was experimentally confirmed. Theoretical relationship between temperature and relative intensities between Li emissions from 671 and 610 nm was derived with consideration of the absorption. Measured number density of Li atom was in the order of 10^{20}-10^{21} m^{-3}.

Keywords: thermal plasmas, plasma diagnostics, lithium ion battery

1. Introduction

Multiphase AC arc is one of the thermal plasma generation methods and have several advantages: high energy efficiency, large plasma volume, slow plasma gas velocity, and low cost. Therefore, multiphase AC arc is expected to synthesis at high productivity. On the other hand, multiphase AC arc is novel generation method of thermal plasma and has some problems: low arc stability, complicated fluctuation, and electrodes erosion. Therefore, further clarification of basic phenomena is needed to realize practical process using multiphase AC arc.

Lithium manganese oxide nanoparticles have been studied as cathode materials for lithium-ion batteries. Nanoparticle synthesis by thermal plasmas has been attracting attention as a method for synthesizing such nanoparticles. Li-Mn composite oxide nanoparticles by inductively coupled thermal plasma has been reported [1]. Nanoparticle production by the multiphase AC arc has also been investigated. Visualization of metallic vapor in the reaction field by high-speed camera with appropriate band-pass filters have recently been conducted. As a result, the temperature field of the reaction field has been successfully evaluated, however the density field has not yet been clarified.

The objective of this study is to establish the method to measure Li atom number density at reaction field from Li self-absorption in multiphase AC arc. Another purpose is to investigate the formation mechanism of nanoparticles in multiphase AC arc.

2. Measurement Principal

Density measurement of Li atom in thermal plasma is established. Followings are assumed to verify measurement principal briefly. Plasma in multiphase AC arc is regarded as uniformed and cylindrical plasma. When this plasma is given an incident light of emission radiance $L(\nu,0)$, the increase in emission radiance $L(\nu,x)$ at position x is the different between emission and absorption and can be calculated from following equation:

$$\frac{dL(\nu,x)}{dx} = \varepsilon(\nu) - \kappa(\nu)\cdot L(\nu,x) \qquad (1)$$

where ε indicates emission coefficient and κ indicates absorption coefficient. They can be calculated with the following equation:

$$\varepsilon(\nu) = \frac{A_{21}N_2 \mathrm{h}\nu_{21}P(\nu)}{4\pi} \qquad (2)$$

$$\kappa(\nu) = \frac{\mathrm{h}\nu_{21}}{c}(B_{12}N_1 - B_{21}N_2)P(\nu) \qquad (3)$$

where A_{21} is transition probability, B_{12} and B_{21} are Einstein coefficients, N_1 and N_2 are number density at each level, h is Plank's constant, ν_{21} is center frequency, c is speed of light. Also, $P(\nu)$ indicates normalized profile, and spectra distribution adapt Lorentzian profile. Therefore, $P(\nu)$ can be calculated following equation:

$$P(\nu) = \frac{\Delta\nu}{\pi\{(\nu-\nu_{21})^2 + (\Delta\nu)^2\}} \qquad (4)$$

where $\Delta\nu$ is half width at half maximum (HWHM) of Lorentzian profile. Assuming that the Boltzmann distribution law, which is an expression for the distribution of the number of particles in excited states, N_1 and N_2 are calculated from the following equation:

$$\frac{N_\mathrm{i}}{N} = \frac{g_\mathrm{i}\exp\left(-\frac{E_\mathrm{i}}{\mathrm{k_B}T}\right)}{Z(T)} \qquad (5)$$

where N is number density, g_i is statistical weight, E_i is excitation energy, $\mathrm{k_B}$ is Boltzmann constant, T is temperature, $Z(T)$ is partition function. In this study, only self-absorption in the luminescence of Li atom used. Therefore, from Eq. (1), the emission radiance at 671 nm, where self-absorption occurs, and the emission radiance at 610 nm, where self-absorption does not occur, respectively are calculated as follow equation:

$$L_{671}(\nu) = \frac{\varepsilon_{671}(\nu)}{\kappa_{671}(\nu)}\{1-\exp(-\kappa_{671}(\nu)\cdot d)\} \qquad (6)$$

$$L_{610}(\nu) = \varepsilon_{610}(\nu)\cdot d \qquad (7)$$

where *d* is plasma diameter. According to Eqs. (6), (7), the theoretical temperature dependence of the relative intensity curves for each Li atom number density was calculated as shown in **Fig. 1**. The theoretical curve was derived assuming plasma diameter of 20 mm. As can be seen from this curve, Li number density can be calculated from temperature and relative intensity of 610 nm to 671 nm. Temperature can be calculated from spectra at 460 nm and

610 nm by relative intensity ratio method. Therefore, Li atom number density can be determined by measuring spectral lines of Li atom at 460 nm, 610 nm, and 671 nm.

3. Experiment Setup

Figure 2 presents schematic image of multiphase AC arc generator. Multiphase AC arc is a device that generates plasma between electrodes by applying AC voltage of different phases to multiple electrodes. Ambient pressure was fixed at 100 kPa. Arc current was adjusted as 120 A. Driving frequency of multiphase AC arc was 180Hz. Six electrodes were introduced from the side wall of the plasma reactor and plasma generated by 6-pahse AC. Argon gas was flowed at 10 L/min from the bottom of the furnace, and Ar shield gas was injected around each electrode at 5 L/min.

The raw materials were injected into the multiphase AC arc by the powder feeder as shown in Fig. 2. Powders of Li_2CO_3 and MnO_2 were selected as raw materials. The composition ratio of Li and Mn was 1:1. The raw materials was fed into thermal plasma region by Ar carrier gas in 10 L/min of flow rate at a feed rate of approximately 0.7 g/min.

Metal vapor was measured with a spectrometer and a high-speed camera. Optical emission spectroscopic measurements were conducted at different observation heights. The observation heights were 30, 40, 50, 60 and 120 mm from the electrode, respectively. High-speed camera observation was conducted from the opposite side of the observation window.

4. Measurement Results

The measured emission spectra with different observation heights are shown in **Fig. 3**. The ratio of the spectral intensities at 610 nm to that at 671 nm suggests that the self-absorption of Li atom is stronger at upstream region than that at downstream region. Li number density was calculated by the theoretical curve shown in Fig. 1.

Calculated temperature and Li atom number density with different observation heights are summarized in **Fig. 4**. The error bars indicate the variation of the data obtained from the optical emission spectroscopic measurements. Result shows Li number density is higher at upstream near the electrodes and tend to decrease downstream. This is because of metal vapor spreading and diffusion or oxidation reaction of Li at downstream.

5. Conclusion

Innovative measurement method of metal vapor density in multiphase ac arc was successfully established. This is important findings for the spatial and temporal analysis of density fields in multiphase AC arc during raw materials supply by high-speed camera. For further development, validation and improvement of accuracy will be conducted.

6. Reference

[1] H. Sone et al., Japanese Journal of Applied Physics, **55**, 7LE04. (2016)

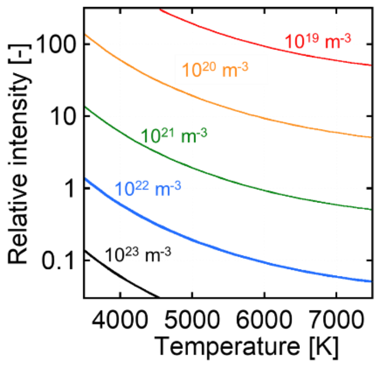

Fig. 1 Theoretical relative intensity of 610 nm to 671 nm as a function of temperature for different lithium atom number densities.

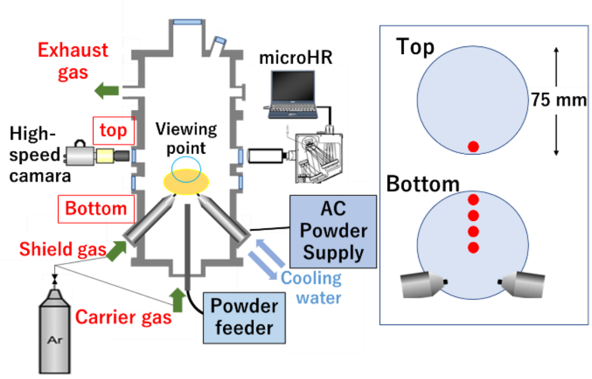

Fig. 2 Schematic image of multiphase AC arc generator. Plot indicates viewing point.

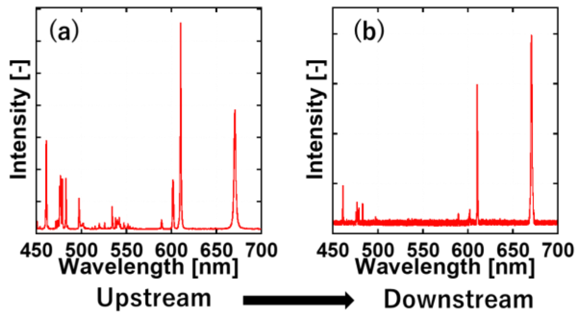

Fig. 3 Emission spectrum of lithium atom obtained at distance of (a) 30 mm, (b) 120 mm from the electrode during powder supply.

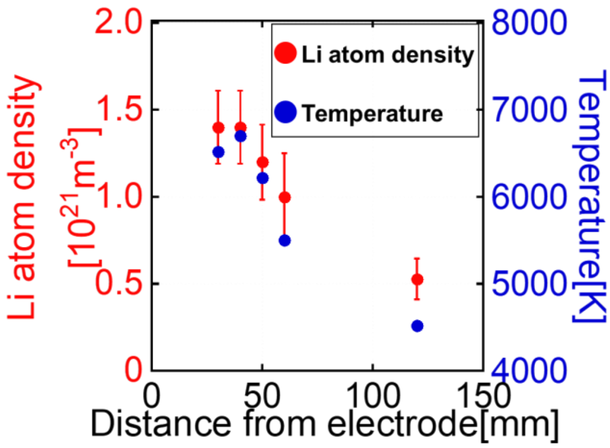

Fig. 4 Temperature and lithium atom density at different observation heights.