Analysis of laser induced plasma of lithium iron phosphate/LiFePO$_4$ using Nd:YAG laser at low pressure

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Abstract. Preliminary analysis of lithium in Lithium Iron Phosphate (LiFePO$_4$) powder using laser induced plasma spectroscopy at low pressure had been done. Recently, LiFePO$_4$-based batteries are widely used in most electric cars and bikes due to less toxic. However, lithium (Li) element is very difficult to detect since it is a very light element. In this work, we used a Nd:YAG laser (1064 nm wavelength, 5 ns pulse width at 10 Hz repetition rate) that was focused on LiFePO$_4$ sample at low pressure. The main Li peak emission in LiFePO$_4$ powder and sheet can be easily detected using this technique. We report the results of experimental study on Li element emission lines at wavelength 460.18 nm, 610.37 nm and 670.83 nm using 2 mJ and 12 mJ laser irradiation at 5 Torr and 35 Torr air atmosphere. The results of this study showed promising application of laser-induced plasma spectroscopy to detect and analyse Li in various samples.

1. Introduction
Laser induced plasma spectroscopy (LIPS) for spectrochemical analysis has actually been an active field of study for decades. Researchers are drawn to the simplicity of LIPS along with its several other advantages. Apart from eliminating the need of tedious sample preparation, spectrum observation can be carried out without the need of sample transport. This method also allows the implementation of local microanalysis and the feasibility of obtaining real time analytical information. Furthermore, this method is very potential for wide range of applications under various operational conditions by improving its sensitivity and accuracy. LIPS consists of direct analysis and indirect analysis. In the case of direct analysis, atomization and excitation take place in one step. In this case, the analytical signal is obtained from the plasma emission by means of emission spectroscopic detection techniques. In the case of indirect analysis, atomization and excitation processes take place separately. Namely, laser plasma is generated only after the atomization process, while the excitation process is subsequently induced by an auxiliary setup to improve detection sensitivity such as inductively coupled plasma spectroscopy. Recently, the use of lasers for material analysis in laser induced breakdown spectroscopy (LIBS) and LIPS significantly grow for various applications. Many books and reports about these techniques are already available [1-4]. LIBS have been continuously improved and applied in industries and research laboratories [5, 6]. The interaction of high-power laser light with a target material has been an active topic of research not only in plasma physics but also in the field of material science, chemical physics and particularly in analytical chemistry.
A lithium ion battery is a device that can convert chemical energy stored in its active materials directly into electric energy by using electrochemical oxidation reduction reactions [7]. Recently, LiFePO₄ has been developed, improved and applied in lithium batteries since it is an excellent material in batteries. Some papers that have been published related to the LiFePO₄, studied about sequential LiFePO₄ particle charge and discharge by conducting electrochemical measurements [8-11]. The grain sizes of LiFePO₄ strongly affect electrode potentials due to the fact that the grain sizes influences electronic contact between LiFePO₄ layer and the current collector [12-13]. Therefore, properties of LiFePO₄ thin film are very important for battery technologies. However, one main problem in characterization of Li thin film occurs. It is very difficult to detect Li content and concentration in material or sample since Li is one of the light elements that cannot be detected by conventional X-ray diffraction spectroscopy. So far, one powerful method to detect Li element in sample is neutron scattering spectroscopy, which is very expensive due to neutron source production. Therefore, a new and alternative method to detection Li is still required. In this work, we propose LIPS as one of the candidates to detect Li element from LiFePO₄ powder sample by utilizing Nd:YAG laser.

2. Experimental setup

Basic experimental setup used in this work is shown in figure 1. The laser source used in this experiment was Nd:YAG laser (Q-Smart 850, 1064 nm wavelength, 5 ns pulse width) operated in the Q-switched mode at a 10 Hz repetition rate. The laser output energy was fixed at approximately 2 mJ and 12 mJ by means of delay switch setting. The laser beam was focused by a lens of focal length f=150 mm onto the sample surface through a quartz window. The diameter of the laser spot on the sample surface was approximately 1.5 mm. The sample was rotated during laser irradiation so that the resulting data represent spatial average of different points on the sample surface. The monitored shot-to-shot fluctuation of the laser was found to be approximately 3-5 %.

There were two samples used in this work. First, Li sheet of LiFePO₄, Second, Li pellet made of LiFePO₄ powder using pellet press machine. Furthermore, the samples were placed in a small, vacuum-tight metal chamber (11.5 cm × 11.5 cm × 11.5 cm). The chamber was evacuated using a vacuum pump and then filled again with air until desired pressure was achieved. The gas flow into the chamber was regulated by needle valves in the air line and pumping line. The chamber pressure was monitored by means of a digital Pirani meter.

Plasma emission was detected by means of a mini spectrometer USB2000 from Ocean Optics, which has an optical fiber input. The optical fiber input was placed at a distance of approximately 10 mm from the sample surface and at a position of approximately 100 mm sidewise from the center of the plasma. The optical fiber position was then slightly adjusted to get the best position. At this position, the fiber is expected to collect most of the emitted plasma.
3. Results and discussion

The first LIPS experiment study was conducted on a lithium sheet sample made of LiFePO$_4$. The resulting emission spectrum presented in figure 2 show three typical Li element emission lines of Li(I) at the wavelength of 460.18 nm, Li(I) at the wavelength of 610.37 nm, Li(I) at the wavelength of 670.83 nm. These three peaks can be clearly detected. An unidentified emission spectrum was also observed in the wavelength regions around 395 nm, 450 nm and 570 nm. These unidentified emission peaks are related to impurities in the samples.

![Figure 2](image)

**Figure 2.** Emission spectrum of LiFePO$_4$ sheets. The laser energies were 2 mJ and 12 mJ and the surrounding air pressure was 5 Torr.

The second experiment was conducted on the Li pellet sample made of LiFePO$_4$ powder. The sample was irradiated using laser Nd-YAG with energy 2 and 12 mJ at surrounding air pressure 5 Torr and 35 Torr. Figure 3 shows the emission spectrum of LiFePO$_4$ pellet.

In the case of LiFePO$_4$ sheet, three typical Li emission lines were detected more clearly than those of LiFePO$_4$ pellet (figure 3). In order to clarify this result, we assume that the atomization process in a thin film sample was easier to proceed than that in the hard bulk or pellet sample [14]. The effect of the sub-target may also occur in this case of LiFePO$_4$ pellet.
**Figure 3.** Emission spectrum of LiFePO$_4$ pellet. The laser energies were 2 mJ and 12 mJ and the surrounding air pressures were 5 Torr and 35 Torr.

Figure 3 shows detail comparison of the intensity-versus-wavelength of three Li lines under different laser energies and air pressures. In the case of pellet sample, when laser energy increased, the emission counts increased as well, so that the correlation between energy and intensity emission is proportional.

### 4. Conclusion

We have shown that three emission lines of Li from LiFePO$_4$ sheet and pellet can be detected using laser induced plasma spectroscopy. In the case of Li sheet sample, the Li emission lines were stronger than those of Li pellet sample even in low energy. It is naturally assumed that in the case of a thin film sample, the atomization will proceed easily, compared to that of a hard bulk sample or pellet. This study can be explored and improved further by varying the number of sample, pressure and energy.

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