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The effect of laser energy on the measurement of oxide stoichiometry of Co_2FeO_4 nanoparticles by atom probe tomography

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Water electrolysis for hydrogen production serves as a critical technology in the renewable energy cycle. However, the efficiency of water electrolysis remains a challenge, predominantly due to limitations in the performance of the anode electrocatalysts where the oxygen evolution reaction (OER) takes place. Therefore, developing high-performance OER catalysts is essential for improving the electrolysis efficiency. Transition metal oxides, e.g., spinel cobalt oxides, have attracted enormous attention due to their promising activity and durability in alkaline condition. Optimization of the electrocatalytic performance of nanoparticles requires a thorough understanding of the structure-performance relationships. In this study, we employed atom probe tomography (APT) [1] to reveal the three-dimensional location of individual elements of Co_2FeO_4 spinel oxide nanoparticles (10 nm in diameter). The measurement of oxide stoichiometry by APT strongly depends on the laser pulse energy and associated electric field [2]. Thus, the aim of this study is to investigate the effect of laser energy on the measurement of oxide stoichiometry of the Co_2FeO_4 nanoparticles.

The Co_2FeO_4 nanoparticles were synthesized by the conventional hydrothermal method [3]. The APT specimens were prepared by focused ion beam milling from a bulk Ni sheet that encapsulates Co_2FeO_4 nanoparticles via a combined electrophoresis and electrodeposition method [4]. The APT experiments were performed at voltage pulsing mode with a pulse fraction of 20%, and at laser pulsing mode with laser energy of 10, 30, 60 pJ, respectively. All APT experiments were conducted in a CAMECA LEAP 5000XR instrument at a specimen temperature of 57 K, a pulse rate of 125 kHz, a targeted evaporation of 5 ions per 1000 pulses.

The results, in Fig. 1, were achieved by exporting the number of ions in the mass spectrum of the APT data of Co_2FeO_4 nanoparticles. Figs. 1a-b show the effects of laser energy on the ratios of M^{1+}/M^{2+} and O_2^{1+}/O^{1+}. The Co^{1+}/Co^{2+} and Fe^{1+}/Fe^{2+} ratios increase as the laser energy increases, suggesting that higher laser energy yields less secondary ionization as the electric field decreases, which is consistent with the trend observed for metals [5] (Fig. 1a). The O_2^{1+}/O^{1+} ratio increases with the laser energy, indicating an enhanced complex ion generation at higher laser energy. Additionally, the O concentration measured at voltage pulsing mode is 40.1 ± 0.4 at.%, and the value increases with laser energy until it reaches a plateau of 46.0 ± 0.1 at.% at 60 pJ (Fig. 1c). Our result shows that the measured oxide stoichiometry is lower than that of Co_2FeO_4. The oxygen deficiency may result from multiple hits, e.g., ${}^{16}O_2^{2+}$ at 16 Da, since the ${}^{16}O_2^{2+}$ complex ions most likely evaporate as multiple hits, similar to ${}^{12}C_2^{2+}$ observed for carbides [6]. To confirm this, the ratio of multiple hits to single hits at 16 Da was plotted in Fig. 1d. The ratio is 13.2:1 at voltage pulsing mode, and it decreases with increasing laser energy, reaching a plateau of 1.9:1 at 60 pJ. This result indicates that the proportion of multiple hits at 16 Da decreases as the electric field is lowed, consistent with previous work [7]. Thus, the increasing O concentration at higher laser energy observed in Fig. 1c is possibly the result of the decrease in the proportion of multiple hits at 16 Da.

In summary, an oxygen deficiency was observed in the APT measurement of oxide stoichiometry of Co_2FeO_4 nanoparticles, possibly due to the multiple events at 16 Da. The proportion of multiple hits decreases with increasing laser energy, which leads to an increase in the measured O concentration.

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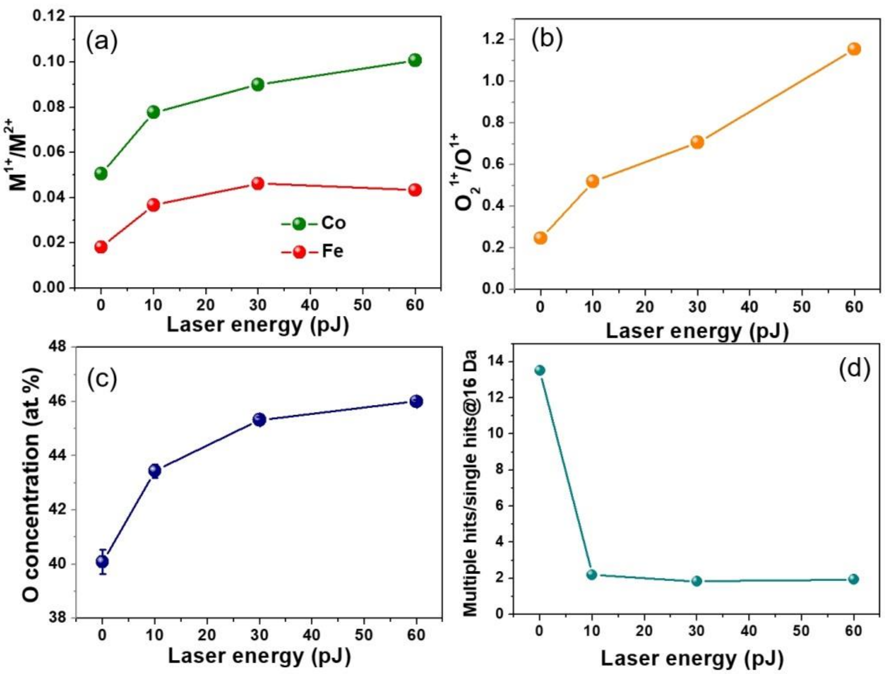

Figure 1. Fig. 1. The effect of laser energy on the (a) M1+/M2+ ratio, (b) O21+/O1+ ratio, (c) O concentration and (d) the ratio of multiple hits to single hits at 16 Da measured from APT data of Co2FeO4 nanoparticles.

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