

Effect of Adding Nanostructured LaGdSmO₂-Based Electrolyte on The Electric Performance of Solid Oxide Fuel Cell

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Abstract— The electrolyte has an inevitable role in solid oxide fuel cell. This work studies and investigates the effect of adding nano-structured of samaria and lanthania on the electric conductivity of (SOFCs). The chemical stability of La_{1-x-y}Gd_xSm_yO₂-(0.5(x+y)-δ) with x, y = 0; 0.1 and 0.2 (LGS) as an electrolyte (SOFCs) was investigated during the electrochemical measurement. At low oxygen, partial pressure (0.003 atm), the LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂ (LS, LG, LGS) electrolyte partly decomposed due to the development of high over potential, and thus the induced reduction atmosphere near the cathode. The morphology of LGS grain near the cathode changed due to the formation of new phases. The main decomposition phases were LaO₂, and LaGdSmO₂. The polarization conductance increased due to microstructural change in LGS and thus the increase in the specific area of the LGS electrode. It is concluded that intermediate operating temperature, high power density and low cost SOFCs can be fabricated.

Index Terms— SOFC(E), LaGdSmO₂, Electrical conductivity(C), Decomposition, Chemical stability

1. INTRODUCTION

Enhancement the performance of Solid oxide fuel cells (SOFCs) is a key problem to generate electricity with little pollution, whoever, the remain the high operating temperature is major problem with that types of fuel cells [1]. In solid oxide fuel cells an electrolyte of ceramic material is used to conduct oxygen ions, its electric conductivity should keep high stability under high operating temperature ranging 600 to 1000 °C [2]. It is commonly made of yttria-stabilized zirconia (YSZ). The required to lowering the temperature of electrolyte is a main and urgent demand in manufacturing art of SOFCs [3-5]. the degradation of A La_{0.8} Sr_{0.2} Ga_{0.83} Mg_{0.17} O_{2.815} (LSGM) electrolyte had investigated in [6-9]. At high temperature, over 1600 °C LSGM easily decomposed because the gallium (III) oxide lowering respect to gallium (I) oxide.

Wan et al. [10] investigated the degradation of LSGM of 30 day test, they concluded that SOFC can be operate at temperature less than 800°C with LSGM as the electrolyte, moreover they concluded that composite material of LSGM 200 μm thick with 20μm LDC buffer layers on either side is very suitable as new electric electrode material.

Wachsman and Lee [11] developed the performance of SOFC electrolyte. They designed a new material electrolyte with high-conductivity and nanostructured electrode to improve the performance to lower operating temperature less than ~350°C, therefore they give other way to convert and store the energy. Many developments on the electrolyte material performance are discussed and investigated in many works [12-14] to enhance and lowering the operating temperature of electrolyte using Nano particles additives or other.

The novelty of the present work is to study performance of electrolyte and cathode with different materials under certain condition.

2. EXPERIMENTAL

Nanostructured samaria-and gadolinia-doped lanthania powders are synthesized at low temperature using a diamine-assisted direct co-precipitation method. A series of four samples are prepared by doping LaO₂ with samaria and gadolinia separately and combined. The general formula of the prepared samples are as follows: La_{1-x-y}Gd_xSm_yO₂-(0.5(x+y)-δ) with x, y = 0; 0.1 and 0.2. Nano-metric powders are prepared. A tetramethyl ethylenediamine (TMEDA) is used as a base in the co-precipitation from nitrate water solutions of lanthania, samaria and gadolinia. Obtained samples (LaGdO₂, LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂) are claimed at 500°C during 6h. Until now, X-ray diffraction analysis, transmission electron microscopy (TEM) analysis and electrochemical characterization have been in the stage of carrying out. Introducing electrolyte materials with higher ionic conductivity carried out to improve SOFC performance at lower temperatures. A candidate for a low- or intermediate-temperature SOFC electrolyte is the LaGdO₂, LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂ (LG, LS, LGS) electrolyte, which has been demonstrated to significantly improve the maximum power density of the SOFC to 0.612 W/cm² at 500 C. These electrolytes are less stable than Yttria Stabilized Zirconia (YSZ), but they have high ionic conductivity. Also, reducing electrolyte thickness can improve SOFC performance. Recent studies in micro-SOFCs demonstrated enhanced reaction and transport kinetics at relatively low temperatures (300-500°C), indicating that high power density, low-temperature SOFC devices may be feasible. The use of microelectromechanical systems (MEMS) processing allows

fabrication of micrometer-thick freestanding SOFC electrolytes, which reduce ohmic losses during fuel cell operations.

3. RESULTS AND DISCUSSION

In the first experiments, suspension plasma spraying was applied using suspensions of SmO₂ particles in saturated aqueous and ethanolic solutions of La salts. The perovskite was formed as the main phase [15], however, La₂O₃ was also observed as an additional phase of significant extent in the coating. Post-treatment with an 80 % oxygen plasma improved the coating purity but the occurrence of detrimental La₂O₃ which reacts to La(OH)₃ causing deeply damage for coating material. Moreover, this method make the coating to get. Layered microstructure returned to the molten particles imposing. The SPS produced coating has very poor porosity, which prevent the gas migration in SOFC cathodes. Although, the TPCVD process can results in highly porous microstructure of LSM, but, the purity of phase was still a problem.

A key parameter controlling the coating purity can be observed in the gradient temperature of plasma jet. When using lanthanum and manganese nitrates (precursors A, B, C and D), the high temperature along the axis of the jet combined with the high volatility of Sm results in a non-stoichiometric composition with regard to La, Gd and Sm in the central part of the coating on a stationary substrate. The deviations from stoichiometry are larger than the perovskite structure can tolerate, thus, the presence of surplus La causes La₂O₃ to appear in the coating beside the desired LSM phase. The cooler outer regions of stationary substrates were always covered with the pure or almost pure perovskite phase.

Figure 1 shows an extreme example of the different phase contents obtained in the centre and in the outer region of a stationary substrate. Scanning of the substrate results in the simultaneous deposition of the two main phases La₂O₃ and LSM. The homogeneity of the perovskite phase could be substantially improved by using precursors with lower lanthanum content, e.g., LaGdO₂, LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂ (precursors A, B and C) or by replacing lanthanum by praseodymium (precursor D), but a completely single-phase, large area perovskite coating could not be achieved. A semi-quantitative method was carried to associate the phase purity of different compounds. It was calculating the percentage of the pure perovskite phase from the intensities of the main XRD peaks of the perovskite and La₂O₃.

Regarding the melting points of the simple oxides of the considered elements, La₂O₃ and SmO show far higher values than the other oxides of Sm, Gd. This leads to the consideration that clusters of La₂O₃ or La-Sm-oxide might form in the hot zone along the plasma jet by homogeneous nucleation similar to the observation made in the system with yttria-stabilized zirconia [7]. These clusters might then be deposited and cannot completely be transformed to the perovskite phase due to the limited interdiffusion of Sm.

Fig. 1 shows a schematic of the scanning electron microscope (SEM) images of the nanostructure. The SEM images demonstrate the feasibility of fabricating with a close-packed array of hexagonal pyramids. The sides of these hexagonal pyramids were approximately 800 nm, and the height of the pyramids approximately 800 nm, providing a corrugated area 1.6-2 times larger than the projected area of the planar structure. The SEM micrographs obtained after electrochemical characterizations exhibited no change in the electrolyte nanostructure. However, consistent with earlier observations, indications of platinum coalescence in the electrode texture were noticed.

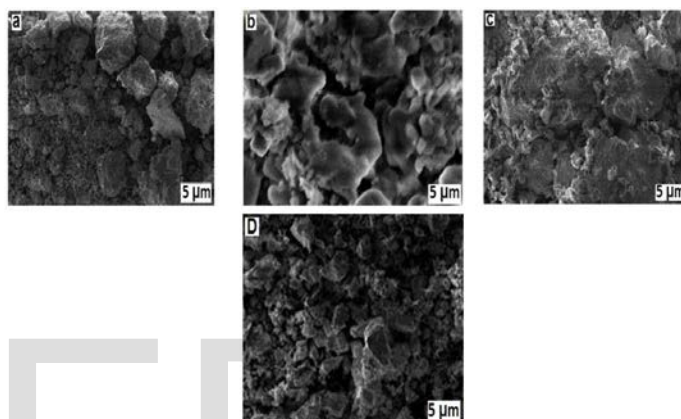


Fig. 1 SEM micrograph of a) LaGdO₂ electrode, b) LaSmO₂ electrode, c) La_{0.6}Gd_{0.2}Sm_{0.2}O₂ electrode, d) La_{0.8}Gd_{0.1}Sm_{0.1}O₂ electrode

Phase purity and crystallographic information of the synthesized LaGdO₂, LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂ perovskite nanostructures were characterized using powder X-ray diffraction. The XRD patterns of LSM perovskite nanostructures synthesized by three methods are shown in Figures 2, 3, 4 and 5. All diffraction patterns of LaGdO₂, LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂ perovskite nanostructures show characteristic peaks of the perovskite phase. The XRD patterns are in good agreement with the standard data for hexagonal symmetry with $a = 5.5163, 6.4532, 6.7653, \text{ and } 6.83242 \text{ \AA}$ and $c = 13.329, 13.435, 14.1232, \text{ and } 14.3103 \text{ \AA}$ respectively. No second phases were observed presumably because a pure phase of LaGdO₂, LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂ (LSM) perovskite was formed at 1250°C [16-21]. In the synthesis of LaGdO₂, LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂ (LSM) perovskite nanostructures the carrier (3, 3', 3''-nitrotripropionic acid was present (NTP)) helped in obtaining a homogeneous mixture of the cations in solution through forming metal complexes, it also helped in the reduction of nitrates in a combustion process, releasing a considerable amount of heat.

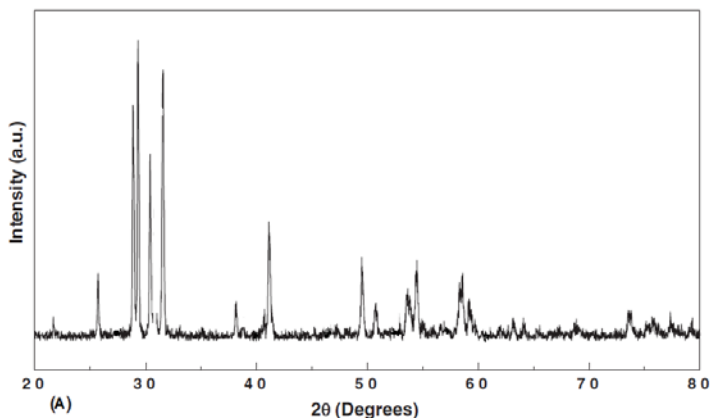


Fig. 2: X-ray diffraction pattern of LaGdO₂ electrode material

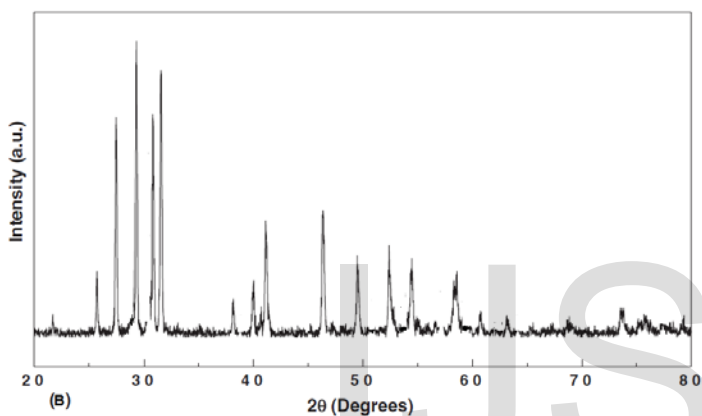


Fig. 3: X-ray diffraction pattern of LaSmO₂ electrode material

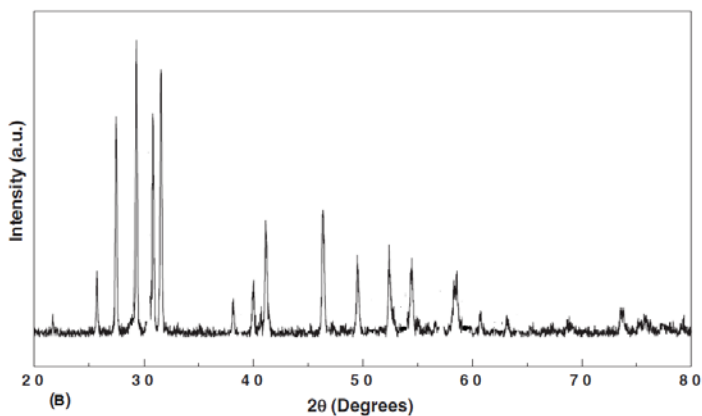


Fig. 4: X-ray diffraction pattern of La_{0.6}Gd_{0.2}Sm_{0.2}O₂ electrode material

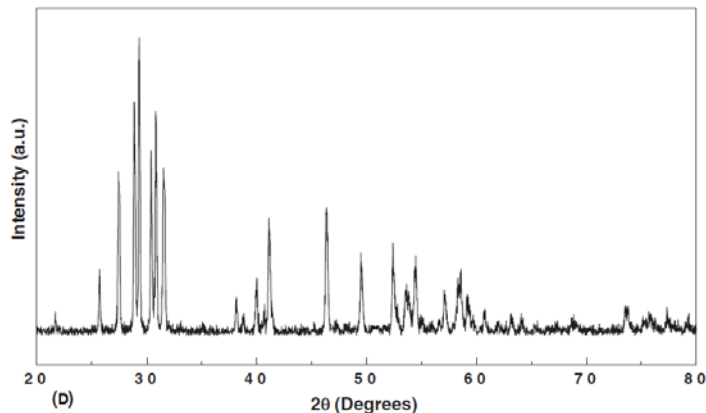


Fig. 5: X-ray diffraction pattern of La_{0.8}Gd_{0.1}Sm_{0.1}O₂ electrode material

Fig. 6,7 (a, b, c and d) show the electrical conductivity of the sample as a function of temperature. It is observed two regions; firstly region I which at $T < 180$ K, this region distinguished by increasing the conductivity with increasing of temperature [22], therefore, the curve is of positive temperature coefficient and has positive electrical activation energy. Secondary the region II which has an opposite of region I, where negative activation energy and the conductivity decreasing with temperature raise at ($T > 180$ K). The Arrhenius equation is expressed as [22];

$$\sigma = \sigma_0 e^{-\Delta E/KT} \quad 1$$

where σ_0 is the initial factor at $1/T = 0$; ΔE is the activation energy, and k is the Boltzmann constant.

The activation energy can be evaluated using this equation by measuring slope of Fig. 6,7. At room temperature, the activation energy and conductivity are shown in Figs. (6, 7).

The negative conductivity of region II can be attributed to the lattice vibration which cause a scattering of carries at elevated temperature. The temperature and activation energy in region II varies widely depend on nature of specimen and structure [14, 23]. If there was a discontinuity in the region curves, this is due to the presence of crystallographic phases or phase transition [24].

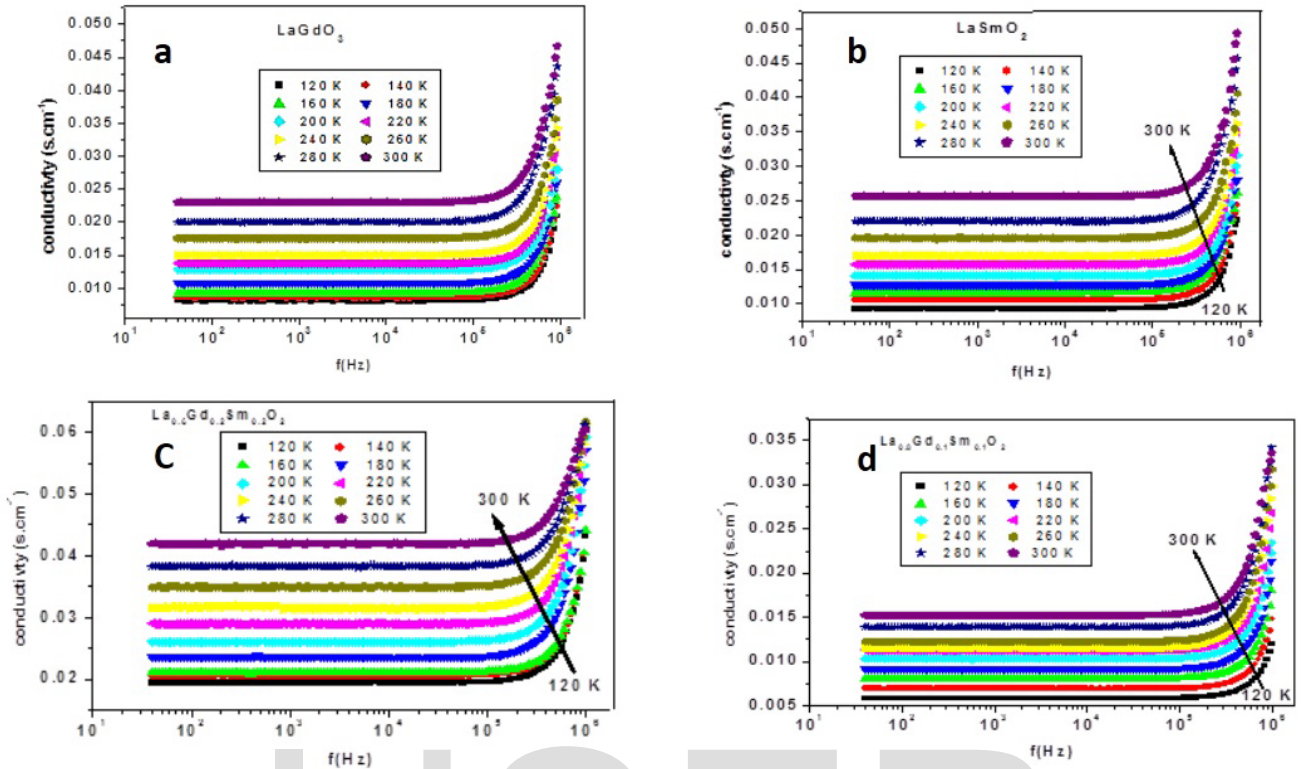


Fig. 6. Frequency dependence of the conductivity of a) LaGdO₃, b) LaSmO₂, c) La_{0.6}Gd_{0.2}Sm_{0.2}O₂, d) La_{0.8}Gd_{0.1}Sm_{0.1}O₂ at 120K to 300K

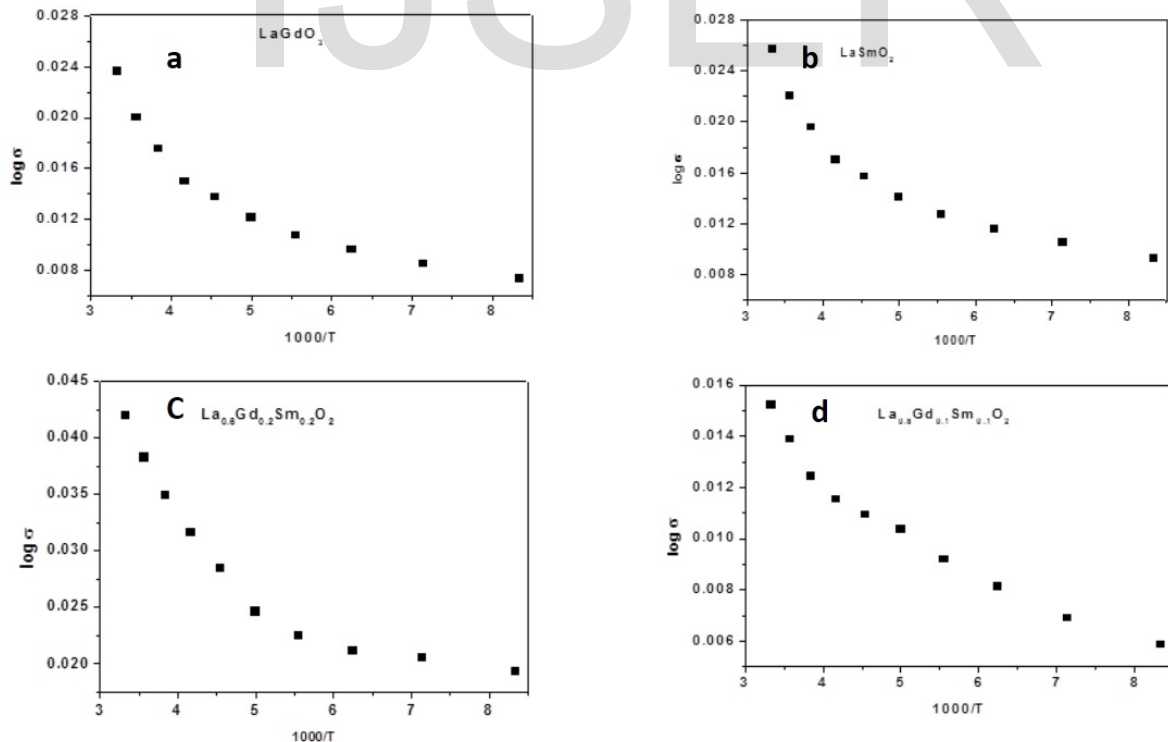


Fig. 7 Variation of the $\log \sigma$ as a function of $(1000/T)$ for a) LaGdO₃, b) LaGdO₃, c) La_{0.6}Gd_{0.2}Sm_{0.2}O₂, d) La_{0.8}Gd_{0.1}Sm_{0.1}O₂

The mechanism of electrical conductivity is hole hops mechanism which localized from one site to other. Or transferring or immigrating [25, 26]. The dependence of the conductivity on frequency can be expressed by the following equation [27-30];

$$\sigma_{tot}(\omega) = \sigma_{DC} + A\omega^s \quad 2$$

where A is a pre-exponential factor and s is the frequency exponent, which generally is less than or equal to one. Fig. 7 (a, b, c, and d) show the frequency dependence of the electrical conductivity at different temperatures. It clearly observed that there is a linear relation between conductivity and frequency. It is concluded that electric contribution has significant effect at low frequencies and high temperature.

4. CONCLUSION

In this work, new proposed materials LaGdO₂, LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂ in nano-size were prepared by chemical precipitation and characterized by X-ray and SEM investigations. A range of perovskite type nanostructures are described, these include nanocomposites materials, which have shown promising properties for their use as cathode materials in SOFCs. The decrease in the nanoscale range is seen to promote not only the increase of active area for the reduction of oxygen, but also allows the tailoring of electrode properties. As the electrochemical and thermo mechanical properties observed in bulk materials are also kept in the nanomaterials, the electrochemical performance of the latest is usually higher than the bulk. In addition, the importance of these nanostructures is expected to increase with the reduction of operating temperatures as limitations ascribed to sintering processes become reduced. According to this fact, nanotechnology is thought to play an important role for the creation of new materials and the optimization of already known ones, promoting significant advances on the development of this environmentally friendly technology. Also, the data obtained from the slopes of the plot of ln σ versus ln(f) for LaGdO₂, LaSmO₂, La_{0.6}Gd_{0.2}Sm_{0.2}O₂, and La_{0.8}Gd_{0.1}Sm_{0.1}O₂ showed that values were decreased as temperature increased. This is the first instance in which the existing ideal SOFC model has been experimentally verified. The promising results suggest that high power density, intermediate operating temperature and low cost SOFCs can be fabricated.

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