



Short communication

Electrocatalytic evolution of hydrogen on a novel SrPdO₃ perovskite electrode

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ABSTRACT

SrPdO₃ was prepared for the first time by the citrate method. XRD, SEM and TGA characterizations were carried out. The catalytic activity toward hydrogen evolution reaction (HER) was investigated, the activation energy, and reaction order and reaction mechanism have been determined using Tafel polarization and impedance techniques. The modified surface showed up to 100 times more efficiency towards electrocatalytic production of hydrogen. Adsorption of hydrogen on the catalyst was the rate-determining step and the reaction order at the surface of the catalyst is 0.86. The molar magnetic susceptibility was measured using Faraday's method and anti-ferromagnetic character was observed.

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1. Introduction

The electrocatalysis in the HER is one of the most important subjects in the field of electrochemistry. Three properties play an important role in selecting catalytically active materials for HER: (a) an actual intrinsic electrocatalytic effect of the material, (b) a large active surface area per unit volume ratio and (c) catalyst stability. Noble metals such as Pt, Pd, Ru, etc. were used in this field. HER starts with the proton discharge (Volmer reaction) and follows either electrodesorption step (Heyrovsky reaction) or the proton recombination step, physical desorption (Tafel reaction). The distinction between steps (1), (2) and (3), as the rate controlling, is usually possible in terms of Tafel slopes or by calculating the rate constants of the forward and backward reactions through simultaneous fitting of polarization and impedance data.

The perovskite type oxides have the general formula ABO₃, with A representing a large cation, usually rare earth ion, while B is the smaller one. For the noble metals incorporated perovskites, an interesting study by Tanaka et al. [1] brought new insight into the behavior of Pd in perovskite structure that Pd could reversibly move into and out of the perovskite lattice to suppress the growth of Pd particles, called self-regeneration of noble metal. Pd in perovskite is reduced under the rich condition, and the reduced Pd metal is oxidized and re-dissolved in the perovskite lattice under the lean condition.

In the present work, SrPdO₃ perovskite was prepared for the first time by citrate method and characterized by XRD, SEM, thermal and magnetic measurements. The catalytic activity toward HER was investigated with the mechanism of the process described.

2. Experimental

2.1. Reagents and equipments

Hexachloropalladic (IV) acid (Aldrich, 99.99%), strontium nitrate, citric acid, nitric acid, sulfuric acid (Aldrich), graphite powder (Sigma–Aldrich, <20 μm, synthetic) and Paraffin oil (Fluka) were used as received without further purification. All measurements were made in oxygen-free solution, which was achieved by continuous purging of the cell electrolyte with nitrogen gas (99.999% pure).

All electrochemical measurements, the Tafel polarization and impedance, were carried out in 0.1 M H₂SO₄ aqueous acid by using a Gamry-750 system. TGA was performed using a Shimadzu TGA-50H instrument. SEM images were obtained by using JEOL JSM-6360LA. While, XRD data analysis was achieved using Proker D₈.

2.2. Preparation of SrPdO₃ by citrate method

Stoichiometric amounts of H₂PdCl₆ and Sr(NO₃)₂ were weighed, dissolved in distilled water, then a sufficient amount of citric acid was added. The pH of the solution was adjusted to 2 by nitric acid. The solution was heated on a hot plate to about 250 °C. The precursor complex undergoes dehydration to produce foam, which

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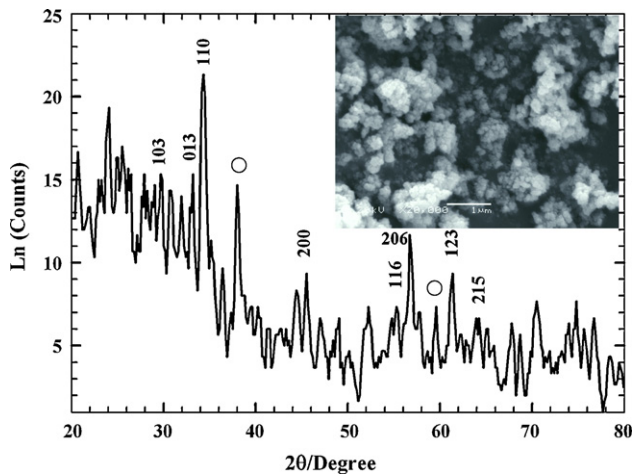


Fig. 1. XRD pattern of SrPdO₃ prepared by citrate method (●) secondary phase, SrPd₃O₄, the inset represents the SEM image, with a magnification of 20,000 times.

then ignited giving a voluminous black fluffy powder. A ceramic nano-SrPdO₃ was obtained by calcinations at 750 °C for 5 h.

Carbon paste was modified by mixing given amount of the perovskite prior to measurements.

3. Results and discussion

3.1. XRD, surface and thermal analysis

Fig. 1 shows the XRD pattern of SrPdO₃ prepared by the citrate method; the inset represents the SEM image. The results suggested successful incorporation of Pd⁴⁺ at the Sr²⁺ cations sites confirming the formation of the orthorhombic phase of SrPdO₃, with the appearance of a secondary phase of SrPd₃O₄. This can be explained on the basis that Pd-containing perovskites were reported to have self-regeneration property [1]. The formation of SrPd₃O₄ was realized by the dissolution of Sr²⁺ and its re-deposition with Pd²⁺ rather than Pd⁴⁺. The average particle size was 35.5 nm as calculated from XRD data. The SEM picture exhibited aggregates with substantial sintering, irregular shape and rough surface.

Fig. 2 presents the TG spectrum of Sr and Pd mixed citrate complex. A smooth weight loss step at 330 °C was attributed to the decomposition of the citrate complex and a sharp weight loss at 750 °C can be assigned to the formation of SrPdO₃.

3.2. Tafel polarization

Tafel linear polarization experiment in 0.1 M H₂SO₄ at the potential region for HER was carried out for unmodified carbon paste electrode (CpE) and CpE modified with SrPdO₃. The presence of the modifier increased the electrocatalytic activity by about 100 times. The values of Tafel slope, exchange current density and transfer coefficient calculated for CpE-containing SrPdO₃ were 871.4 mV decade⁻¹, -946.3 μA cm⁻² and 0.07 respectively. According to the general HER mechanism in acidic media [2], this Tafel slope value indicated that the Volmer reaction step i.e. adsorption of hydrogen on the catalyst was the rate-determining step.

The order of the reaction with respect to H⁺ was determined at constant ionic strength of the solution by varying the H₂SO₄ concentration keeping the ionic strength constant with Na₂SO₄. Fig. 3 shows the dependence of the cathodic current response on the H⁺ ion concentration. The reaction order (the slope) for SrPdO₃ was 0.86. The fractional reaction order was expected for HER catalyzed by oxide catalysts.

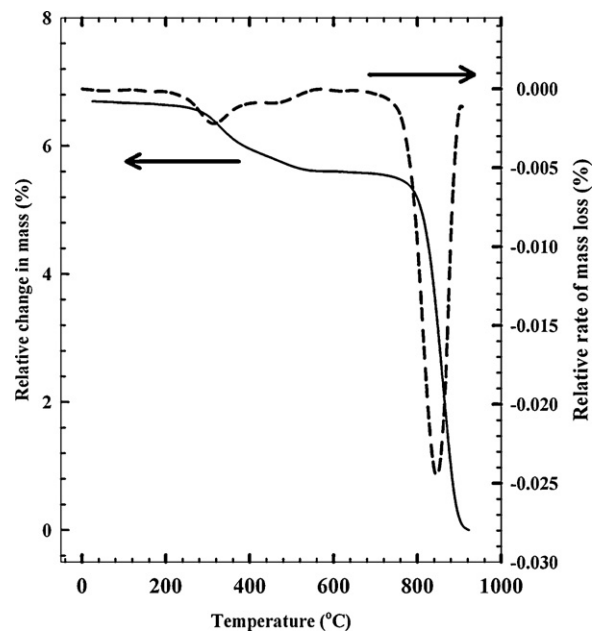


Fig. 2. TG spectrum of Sr and Pd mixed citrate complex, heating rate was 10 °C min⁻¹.

In order to evaluate the temperature effect on the kinetics of HER for SrPdO₃, Tafel linear polarization measurements were performed in a temperature range of 298–338 K. Fig. 4 shows a set of Tafel curves recorded on CpE modified with SrPdO₃ at various temperatures, the inset represents Arrhenius plot. The activation energy value for SrPdO₃ is 27.9 kJ mol⁻¹.

3.3. Electrochemical impedance spectroscopy (EIS)

EIS measurements were performed over a frequency range from 100 kHz to 10 mHz at selected overpotentials from the Tafel polarization curves. The EIS spectrum revealed the presence of two time constants. EIS data were modeled using non-linear least-squares fit analysis (NLLS) software and electrical equivalent circuit. A good agreement between the experimental and simulated data was obtained when the equivalent circuit shown in Fig. 5, the inset, was used to describe the EIS response of the electrodes. The dependence of each electrical equivalent circuit parameter on applied overpotential was investigated. Fig. 5 shows a set of EIS spectra recorded on CpE modified with SrPdO₃ at various overpotentials. The figure shows that the radius of the high-frequency

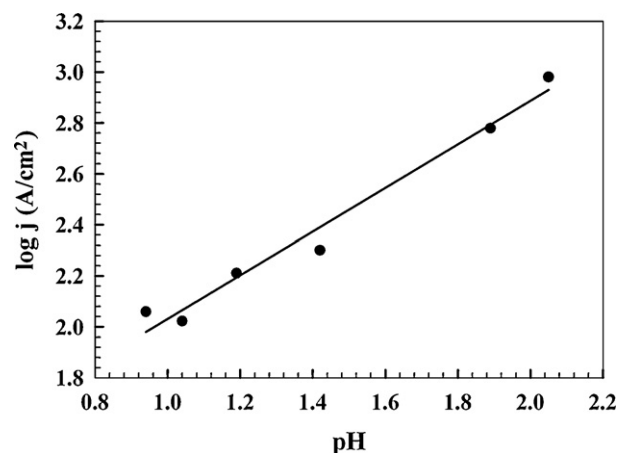


Fig. 3. Plot of log *j* vs. pH (at -0.6 V) for determination of the reaction order.

Table 1
The electrical equivalent circuit parameters calculated from the NLLS analysis for SrPdO₃.

η (V)	R_s (Ω cm ²)	CPE1 (F cm ⁻²)	m	R1 (Ω cm ²)	CPE2 (F cm ⁻²)	n	R2 (Ω cm ²)	Z_w (Ω s ^{-1/2})
-0.050	16.1	26500	0.83	13.2	26340	0.85	85.3	17.9
-0.075	17.9	28350	0.87	15.9	22810	0.91	85.2	10.4
-0.100	16.6	30330	0.84	13.3	28850	0.87	86.6	13.9
-0.125	18.7	31160	0.84	14.7	23000	0.89	71.9	9.9
-0.150	16.5	50390	0.98	5.6	28070	0.85	70.9	5.7

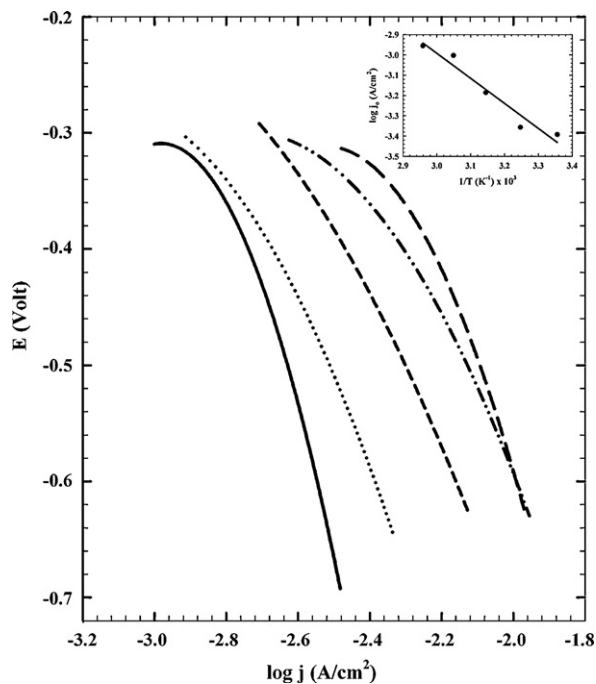


Fig. 4. Linear Tafel polarization curves for the HER recorded on CpE modified with SrPdO₃ in 0.1 M H₂SO₄ at various temperatures; scan rate = 1 mV s⁻¹, the inset represents the Arrhenius plot (—) 298 K, (— — —) 308 K, (---) 318 K, (● — ●) 328 K, and (---) 338 K.

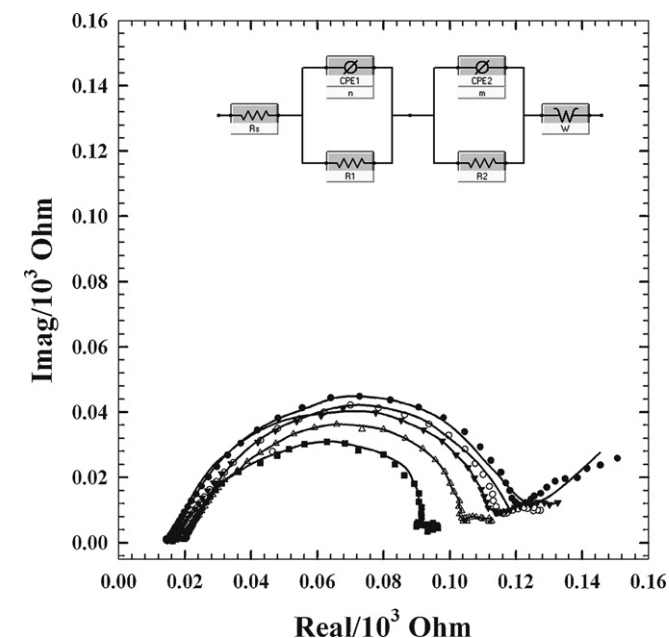


Fig. 5. Nyquist plots showing EIS response of CpE modified with SrPdO₃ in 0.1 M H₂SO₄ at various HER overpotentials, symbols are experimental and solid lines are modeled data (●) 50 mV, (○) 75 mV, (▼) 100 mV, (△) 125 mV, (■) 150 mV, the inset represents electrical equivalent circuit.

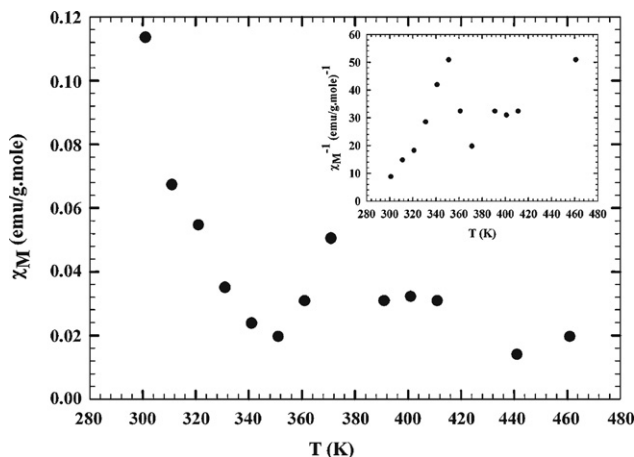


Fig. 6. The dependence of the molar magnetic susceptibility on the absolute temperature at a magnetic field intensity of 1990 Oe for SrPdO₃, the inset represents the Curie–Weiss plot.

semicircle (smaller semicircle) is potential independent; it can be related to the electrode surface porosity response. On the other hand, the radius of the low frequency semicircle (larger semicircle) decreases with an increase in overpotential that is related to the charge-transfer resistance process and double layer capacitance. [3,4]. Table 1 shows the electrical equivalent circuit parameters calculated from NLLS analysis. With an increase in overpotential, CPE1 increased and R1 decreased. Therefore, CPE1 and R1 are related to the HER charge-transfer kinetics, namely to the response of double layer capacitance characterized by CPE1 and HER charge-transfer resistance characterized by R1. Contrary to the behavior of CPE1, the value of CPE2 is relatively constant while the value of R2 decreased. This is a typical behavior related to the porosity of the electrode surface. The value of the Warburg component, related to the diffusion of the H⁺ ions, decreased with an increase in overpotential.

3.4. Magnetic measurements

The dependence of the molar magnetic susceptibility (χ_M) on the absolute temperature at a magnetic field intensity of 1990 Oe for the sample SrPdO₃ is shown in Fig. 6, the inset represents the Curie–Weiss plot. The investigated sample has an anti-ferromagnetic character with Neel temperature ($T_N = 370$ K). The value of χ_M decreases sharply with increasing temperature up to about 350 K after which it increases with temperature giving a hump at the Neel temperature of 370 K, after that, a paramagnetic region is obtained. The calculated magnetic moment (μ_{eff}), the Curie constant (C) and the Curie–Weiss constant (θ) were 5.7 B.M., 4.1 (emu/g mol) K and -56.7 K. The negative value of (θ) agrees well with the anti-ferromagnetic character of the sample.

Conclusion

SrPdO₃ was successfully prepared for the first time by the citrate method. SrPdO₃ exhibited a high catalytic activity toward the HER. The calculated activation energy for SrPdO₃ is 27.9 kJ mol⁻¹. The

prepared perovskite has an anti-ferromagnetic character with Neel temperature, $T_N = 370$.

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