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Perovskite and Ferrite based nanocomposite for electrocatalytic production of hydrogen

A dissertation submitted in the partial fulfillment of
the requirement for the degree of
Master of Science
in
Chemistry

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DECLARATION

I declare that the thesis entitled "**Perovskite and Ferrite based nanocomposite for electrocatalytic production of hydrogen"** has been prepared by me under the supervision of **Dr Jimmy Mangalam and Prof Sanjeev Dubey** from **Department of Chemistry, School of Engineering, University of Petroleum & Energy Studies, Dehradun, India.**

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I certify that, **Anirudh Shaji** has prepared his project entitled **"Perovskite and ferrite-based nanocomposite for electrolytic production of hydrogen"** for the award of **M.Sc. Chemistry**, under my/our guidance. He has carried out the work at the **Department of chemistry, School of Engineering**, **University of Petroleum & Energy Studies, Dehradun, India.**

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Abstract

The growing importance of production of clean fuel is important. The purpose of this study was to come to a conclusion weather or not a composite made from of perovskite (strontium titanate) and a ferrite-based (nickel ferrite) material can be used as a suitable electrode in a electrochemical reaction that involves the splitting up of water. Based on literature, nickel ferrite and strontium titanate showed the best of interest towards the objective. The individual components were made and the composite was prepared, and characterized using FT-IR and XRD spectroscopy.

Keywords: XRD, Clean production of fuel, strontium titanate, nickel ferrite, Electrochemical reaction

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1. Perovskite and Ferrites

1.1 What are perovskites

Fig 1. *Natural perovskite*

Materials that are having a chemical formula of ABO_3 or AB_2O_4 are identified as perovskites. It was first discovered in the Ural Mountains by Gustav Rose from Russia however the name was later given by mineralogist Lev Perovski. The first discovered perovskite was calcium titanium oxide which got the name of true perovskite. Usually, they serve for their vivid catalytic properties, they also provide superconductivity. The structure includes a 15 centred cubic cell out of which the cations are located at the corners of the cube, the oxygen atoms are present at the phase centre of the cube while second cations are located at the octahedral position of the cube given.

<u>Structure</u>

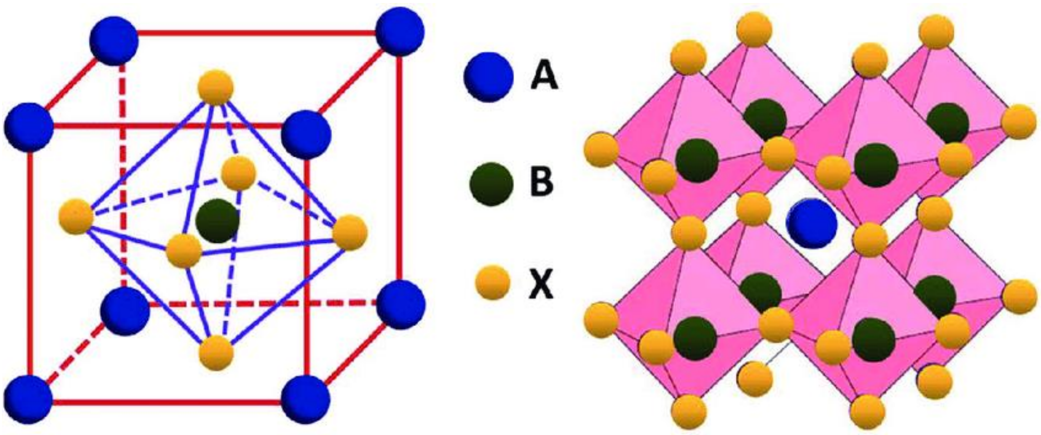


Fig2. *Structure of perovskite*

The structure of perovskite consists of a 15 cubic lattice structure among which there are 2 cations present (different size) and one anion. One cation is located at the edges of the cube or the corners of the cube, while the other one Is present at the octahedral positions of the cube. The anion is present at the centre of the cube itself. If we take an example of calcium titanium oxide, we can see that calcium is present at the corner of the cube while the titanium ion is present at the octahedral positions and the oxygen anion are present at the body centre of the cube. The colour and nature of the perovskite can vary with the impurities that are present within the compound hence various changes can be made by modifying the structures or by introducing certain impurities

1.2 What are ferrites

They have the general formula of AB_2O_4. They have a spinel structure. We are adding ferrites to perovskite so that it can increase the feasibility of the material formed. It also reduces the electrical input taken which further can reduce the cost as well.

Structure

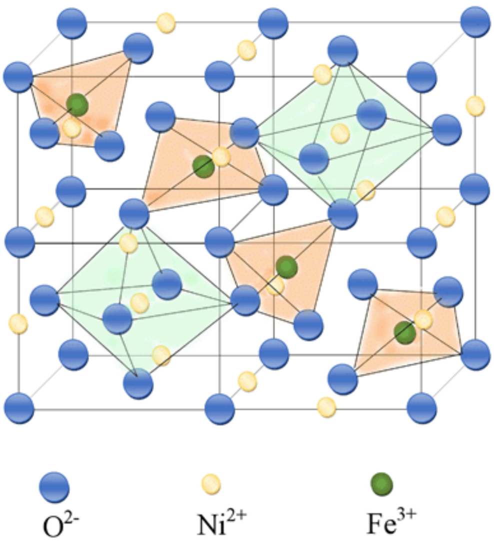


Fig3. *Spinel structure of ferrite*

The nickel ferrite compound exists as a spinel compound itself under a general formula of AB_2O_4 structure. Sometimes this spinel structure can be changed to inverse spinel as well where half of the octahedral occupying voids will be transferred to the tetrahedral void which will make the structure inverse spinel and have a general formula of $BAB(O_4)$.

1.3 Why do we need to produce hydrogen

The increasing demand of hydrogen has led to many new innovations, the need for producing hydrogen is growing by the minute. It produces nearly no waste materials when combusting (water is produced), also it is abundantly available which leads to its demand on field.

Fig4. *Hydrogen uses*

1.4 Why electrocatalysis

Although there are numerous ways by which hydrogen can be produced electrocatalysis is one of the most clean and efficient way to produce hydrogen gas. The problem there arises where low-cost catalyst is required, at the moment catalyst like platinum is used which is highly efficient but at the same time costly. On the other hand, the fusion based product of perovskite and ferrite have lower cost and is still highly efficient.

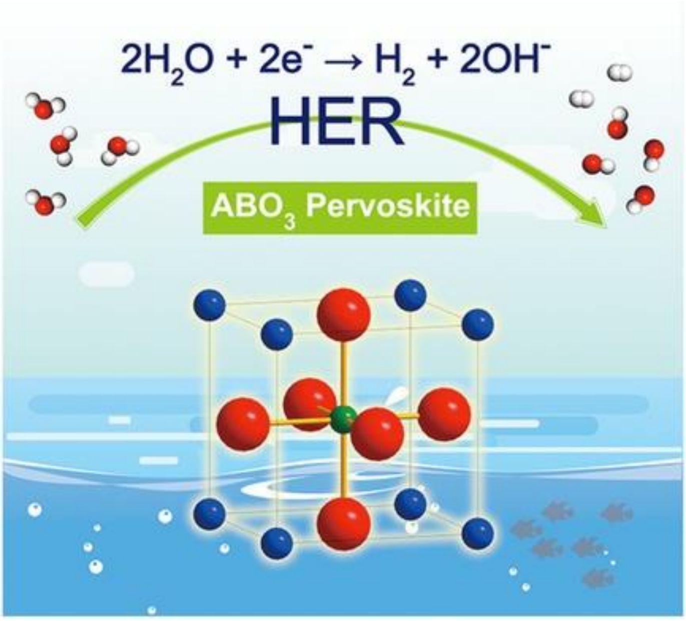


Fig5. *electrocatalysis*

1.5 Different methods to produce hydrogen

1.5.1 Thermochemical process

Energy that has been accumulated from various resources such as natural gas; biomass have been directed towards the release of hydrogen from their molecular structure. In some cases, heat is imparted over closed chemical cycles and then hydrogen is produced. The temperature can reach up to 2000 degree Celsius.

1.5.2 Electrolytic process

This technique is available very easily and it uses electrolyzers to separate water into hydrogen and oxygen. Electrolysis is a method that is used to separate water into its individual components of water and hydrogen with the help of electricity. The reaction takes place inside a unit called as electrolyzer. Each of the unit contains a anode and a cathode along with a electrolyte that separate's it.

Types: -

polymer electrolyte membrane – water will react at the anode and form oxygen along with hydrogen ions. Then the hydrogen ions produced will move selectively from the anode through the electrolyte towards the cathode. At the cathode hydrogen will join with the electrons and form hydrogen gas

Alkaline electrolyzers – In this type the hydrogen gas will be evolved at the cathode, while the electrolyte used will be a alkaline solution or sodium or potassium electrolyte.

Solid oxide electrolyzers – The reactions occur at 700-to-800-degree higher temperature than polymer electrolyte membrane.

1.5.3 Biological process

In this method certain microbes are used to produce hydrogen via biological process. The reactions can include the use of sunlight or any other chemicals along with that. The further stages and methods are still being discovered.

CHAPTER 2
EXPERIMENTAL DETAILS

1. Synthesis of Materials

1.1 Synthesis of strontium titanate

The precursors used here are strontium nitrate and titanium isopropoxide. Strontium nitrate Is taken in a quantity of 2.5 millimoles in 50ml of water and 0.395 gm of titanium isopropoxide was mixed with 10 mL of ethanol. These both solutions were then mixed and allowed to stir continuously at room temperature for about 4 hours. Sodium hydroxide was added at a regular interval of 10 minutes each after allowing the initial stirring of 1 hours. After the pH had become 12, the sample was taken out and was filtered with the help of a Whatman filter paper. The sample was then dried in the oven for about 2 hours then kept in the muffle furnace for 4 hours respectively.

1.2 Synthesis of Nickel Ferrite

The precursors used here are nickel nitrate and ferric chloride. Both nickel nitrate and ferric chloride were prepared along the concentration of 0.2M. sodium hydroxide was also prepared which was having a molar concentration of 0.5M. Both the solutions were then mixed with equal amounts of 40ml each and then was kept on a magnetic hot stirrer plate which was allowed to stir for around 2 hours after which sodium hydroxide was added until ph changed to 12. The sample was taken out and filtered, after which it was kept in the oven for about 2 hours and later on in the muffle furnace for about 4 hours respectively.

1.3 Synthesis of composite between strontium nitrate and nickel ferrite

Here both the samples of nickel ferrite and strontium titanate is used as the precursor. While the preparation of strontium titanate is being done, we add around 2mg of prepared nickel ferrite into the process and then continue by adding sodium hydroxide for faster precipitation. The compound is then taken out and is then kept in the oven after which it is kept in the muffle furnace for 6 hours.

2. Charecterization technique (XRD and FTIR)

2.1 XRD

X ray diffraction technique is a non-destructive analytical method used to analyze the composition, crystal structure and so on. There can be many types of materials out of which some maybe single phase and some maybe having multiple phases. The instrument used for XRD is x ray diffractometer in which different phases of a particular compound can give different refractions. The basic working principle of a diffractometer is that a source is used to illuminate the sample and then the diffracted light enters or is collected by the detector.

Some of their applications include – analysis of phase change, analysis of physical properties, the main use is for the qualitative and quantitative analysis of pure substances and mixture

Fig6. *X ray diffractometer*

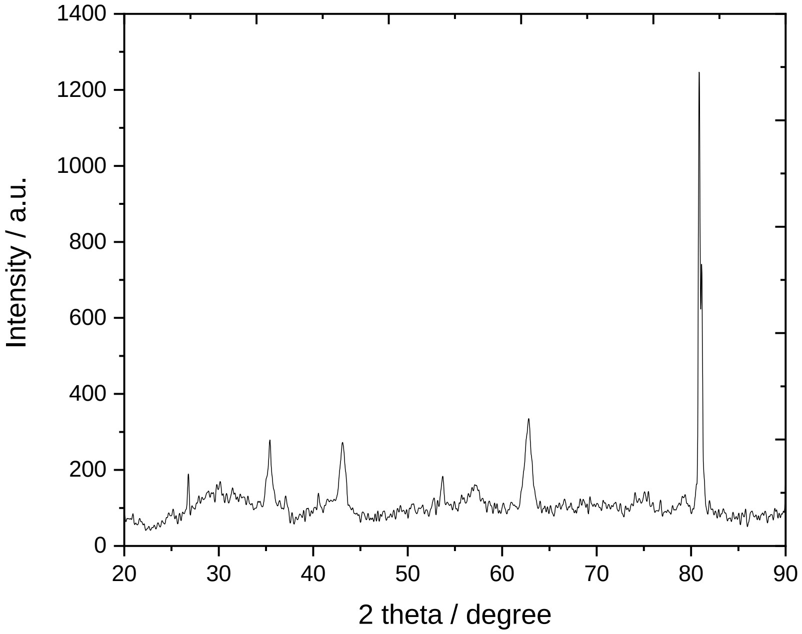
2.2FT-IR

This technique is a non-destructive method and is widely and mainly used to find out the chemical composition of a particular compound. The basic working principle of FT-IRmethod is it finds out the vibrational states either bending or stretching of the molecules. It is used to find out which functional group is present within the sample provided

Fig7. *Alpha 2 compact FT IR*

3. Analysis of the compound

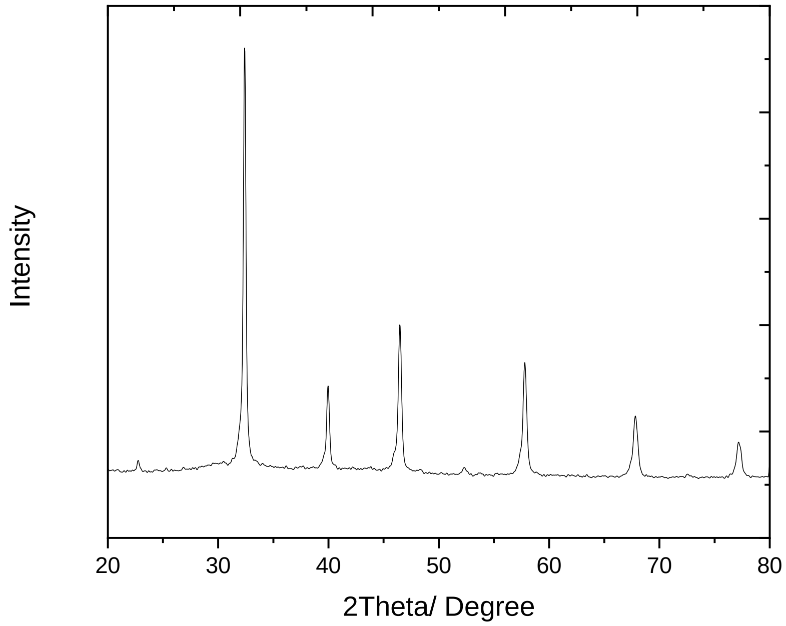
3.1 XRD of nickel ferrite



2theta	(h,k,l)
35.415	3,1,1
43.107	4,0,0
62.735	4,4,0

Among these there is another peak at (2theta = 81.145) this peak indicates the presence of nickel oxide that indicates that the reaction time along with certain parameters should change.

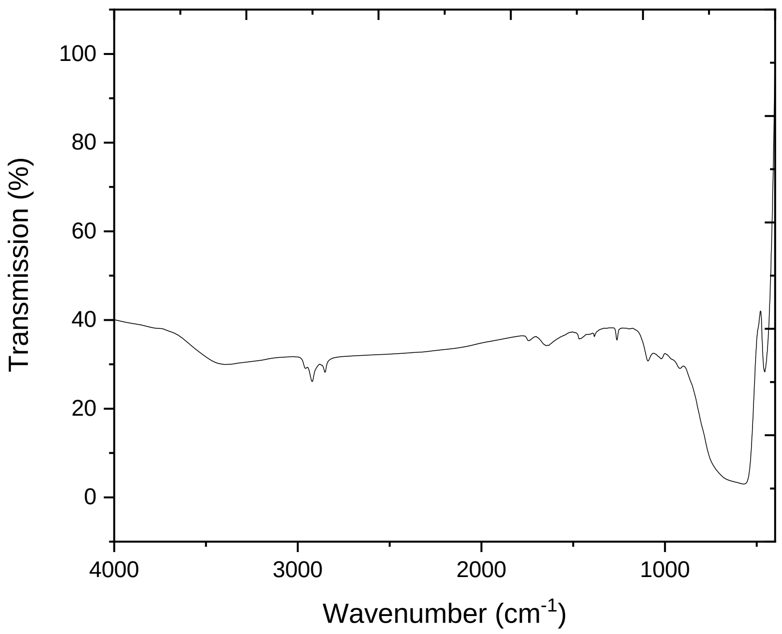
3.2XRD of strontium titanate



2theta	(h,k,l)
32.397	1,1,0
39.913	1,1,1
46.475	2,0,0
57.789	2,1,1

The above theta values to which the corresponding values indicated that the compound was formed.

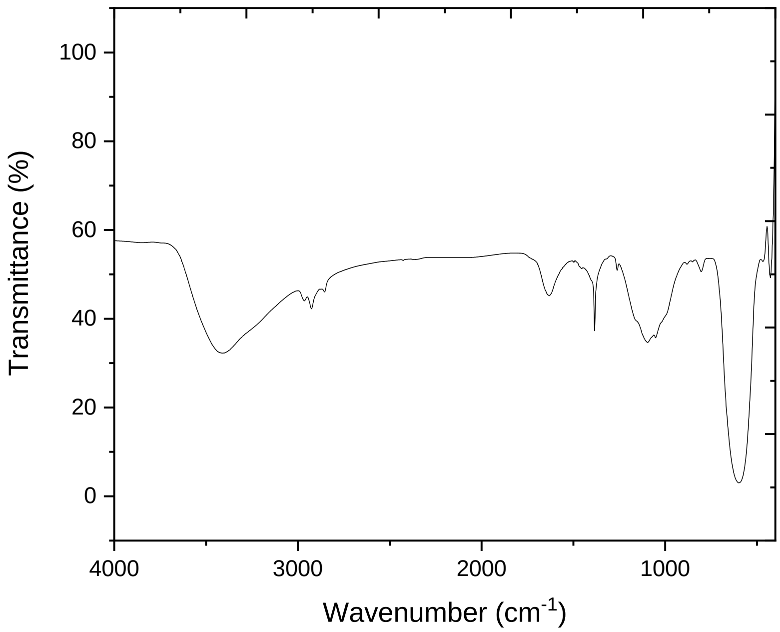
3.3FT-IR of Strontium titanate



Peaks observed	functional groups
452	Ti-o
574	Ti-o

The peaks corresponding to the above-mentioned ones shows formation of metal oxygen bond which in this case is titanium oxygen bond. There is also less amount of water content in the sample.

3.4 FT-IR of nickel ferrite



Peaks observed	functional groups
603	Ni-o
1386	o-h
3419	Ni-o

The peaks observes at 603 and 3419 indicated the formation of nickel oxygen bond stating the formation of the compound.

CHAPTER 3
RESULTS AND CONCLUSIONS

1. Report Analysis (XRD)

1.1 Strontium titanate

The XRD report shows excellent formation of the compound and when compared with the peaks of an ideal report shows good comparison in peaks

1.2 Nickel ferrite

The XRD report shows the formation of the compound is still underway, there is a high peak at theta= 80 which indicates the presence of nickel oxide that indicates that the reaction has not completely taken place. Further changes in parameters are required that include increased temperature, extended reaction time and further on for proper formation of the compound.

2. Report Analysis (FT-IR)

2.1 Strontium titanate

The amount of water that was present in the sample was reduced on a significant amount. This was done by extending the drying conditions that was changed from 4 hours to 8 hours. The metal oxide bonds could be found within the range below $1000cm^{-1}$ this was observed when compared with the one of the original compounds.

2.2 Nickel Ferrite

The amount of water that was present was reduced. This was also done when the drying time was increased by almost double the time. The metal oxide bond was observed in the area below 1000^{-1}.

Conclusions

The compounds prepared which were strontium titanate and nickel ferrite out of which strontium titanate was formed and nickel ferrite was formed but was not clearly formed as there was some amount of nickel oxide in it that indicates some parameters had to be changed like increasing both reaction time and temperature provided. The composite was also prepared but was still unable to be tested.

REFERENCES

- Zhang L, Mei L, Advanced applications of perovskite materials, nano micro letters (2023)

- Mohammed, low temperature preparation, characterization, magnetic properties, thermal optical and morphological properties of nano size single phase nickel ferrite, journal of material science, materials in electronics, 28(18), 2017

- Shan Wang, Aolin Lu, Chuan- Jian Zhong, Hydrogen production from water electrolysis and role of catalysts, nano convergence (8), 2021

- Ibukun Oluwa Seun, Onome Ejeromedoghene, Sheriff Adewuyi, Electrochemistry and electrocatalysis of hydrogen generation using hexa coordinated nickel-based complexes, catalysis communications, volume 179, 2023

- Narang S.B., Pubby K, Nickel spinel ferrites a review, journalism of magnetism and magnetic matter, 2021