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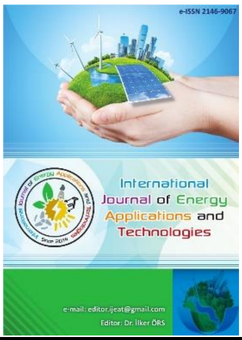

Review Article

Review of lithium-ion, fuel cell, sodium-beta, nickel-based and metal-air battery technologies used in electric vehicles

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ABSTRACT

Interest in electric vehicles (EV) or hybrid electric vehicles (HEV) is increasing day by day. These vehicles have many advantages as they operate more efficiently and do not cause noise or environmental pollution compared with conventional vehicles. However, it has some disadvantages. For some, it is the most important trust issue. An important criterion is that the daily vehicle cannot go to a sufficient range. Therefore, vehicle designs and applications continue to be made with high energy and power distribution, low performance, and high efficiency ESSs using two or more energy storage systems (ESS). In addition, lithium-ion batteries are widely used in EVs and HEVs. Although they have high power and energy estimations, their high duration, short freezing life or service life, and insufficient efficiency are the guides for executing different alternative solutions. The aim of this article is to create a different perspective by including unusual battery types and fuel consumption technology known as clean energy sources. The Zero Emlu Battery Research (ZEBRA) battery, which is seen as a future technology in EVs and HEVs in this article, features such as the operating principle of the nickel-based battery structure (Nickel-Cadmium, Nickel-Iron, Nickel-Zinc), operating temperature ranges, cycle lifetimes, and service lives. In addition to the lithium-air battery, which is a metal-air battery technology and is seen as a source of hope with its high energy densities in the future, it is also included. Comparisons between these batteries were made, and their applicability in HEVs and EVs was examined.

Keywords: Electric vehicle; ZEBRA battery; Nickel-based batteries; Metal-air batteries; Fuel cell

1. Introduction

Greenhouse gas (GHG) emissions are particularly noteworthy because of their environmental impact. The large number of greenhouse gasses (particularly CO_2) in the atmosphere can cause additional heat retention, causing global warming [1]. According to a report by the European Union, which reported that more than 70% of the emissions from the transportation sector belong to road transport, the transport sector is responsible for approximately 28% of total CO_2 emissions [2]. It has been determined that the most effective and practical way to reduce GHG emissions is to use EVs and HEVs instead of traditional internal combustion engine (ICE) vehicles [3]. For this reason, there are currently many attempts to switch from fossil fuel-based vehicles to battery electric vehicles (BEVs). Accordingly, it has been announced that the European Union achieves more than 80% of all electric vehicles by 2030 [1].

Figure 1 shows the estimated annual demand for EVs worldwide [4]. Analyzing this figure, it can be seen that the annual demand for EEs has increased by 31% per year until 2020. This forecast chart also shows that EV production is expected to grow to over 55 million in 2037, more than double the current production [5].

Mohammadi stated that ESSs are the most important component of EVs [5]. In addition, electric motors and battery technologies are seen as key factors affecting the range and performance of EVs. Among them, batteries are among the most expensive parts of EVs as they directly affect their performance [6]. In addition, ESS has several disadvantages, including low power density, battery life, and high cost. These limitations constitute a factor for developing alternative strategies [7-10]. For example, the recharge time of batteries used in EVs is 6-12 h. However, the recharging time for fuel cell electric vehicles is approximately 5–7 min [11]. According to these data, the range problem in EVs can be overcome with fuel cell vehicles. These EVs, which are similar to conventional vehicles, will can cover kilometers without any problems.

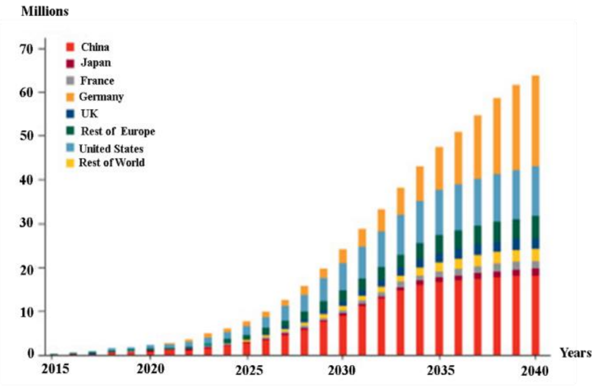

Fig. 1. Estimated annual demand for EVs worldwide [4]

Lithium-ion batteries are preferred compared to other batteries used in EVs because of their features such as high energy densities, high operating voltages, low self-discharge rate, long lifetime, and almost zero memory effect [12].

Lithium–air batteries (Li-Air) operate at higher temperatures and have higher specific energy and power. Therefore, these batteries were found to be superior to lithium-ion batteries [13-14]. However, there are continuing problems in the practical application of lithium-air cells. Therefore, its use is prevented [6]. However, two of the most promising metal-air battery systems are Zn-air and Li-air batteries.

After the Ni-MH battery entered the EV field, another alternative battery that followed the Ni-MH battery was investigated. This is the sodium–nickel chloride (Na-$NiCl_2$) or ZEBRA battery. This battery is generally used in public transportation such as busses or minibusses because of its high operating temperature (250-350 ℃) [15]. In addition, a comparison was made with at lead-acid battery. As a result, it has been determined that it has a much greater performance than the lead-bearing battery.

In this study, lithium-ion batteries, sodium sulphur (Na-S), ZEBRA batteries from nickel-based batteries, and metal-air battery technology have been examined. In addition, fuel cells, known for their high energy densities and efficiencies, have been recently studied in EVs and HEVs. In these reviews, the working principles, power and energy densities, cycle life, charge-discharge times, and efficiency of ESSs used or continuing to be researched in EVs and HEVs have been considered. According to the results obtained, the appropriateness of its use in EVs and HEVs was evaluated.

2. Lithium-Ion Batteries

The use of LA and Ni-MH batteries in energy storage and electromobility has shifted to lithium-ion batteries since 2010 [16]. As a result of the rapid development of EVs, the global demand for power batteries has also increased exponentially. Because of the increase in this demand, it has been determined that international transportation has increased approximately 20 times in the last five years [17, 18]. A lithium-ion battery consists of an anode, cathode, separator, and electrolyte. Depending on the application, at the anode of a state-of-the-art lithium-ion battery, graphite (with alloy materials), amorphous carbon (hard and soft carbon), silicon-based compounds, or transition metal compounds (eg lithium titanate) are used [19]. The particular focus of these batteries is the cathode materials. These cathode materials, most in varying concentrations, consist of lithium, nickel, manganese, and cobalt [20]. The focus is on this material because the cathode materials of lithium-ion batteries account for more than 20% of the total cost. It is also an important factor in determining the energy and power density of the battery. Some commonly studied cathode materials for lithium batteries are $LiCoO_2$, lithium manganese oxide ($LiMn_2O_4$), and $LiFePO_4$ [21].

Figure 2 shows the operating diagram of the lithium-ion battery. During the discharge process, Li+ ions are transferred to the separator using electrolyte material to reach the cathode from the anode. After this process, electron loss occurs at the anode and the oxidation reaction occurs. At the cathode, a reduction reaction occurs, and a lithium metal oxide compound is formed. During the charging time, the opposite of this process occurs. In lithium-ion batteries, electronic controllers are used to prevent negative situations such as explosions due to overcharging and overheating [22]. Commercially used lithium-ion batteries are classified into five categories [23]. These are a) $LiCoO_2$ (LCO), b) $LiNixCoMnO_2$ (NCM), c) $LiNixCoyAlzO_2$ (NCA), d) $LiMn_2O_4$ (LMO), and e) $LiFePO_4$ (LFP) batteries. NCA and NMC are high energy density batteries [24]. Therefore, they are widely used in EVs. Interest in these two high-tech batteries is increasing.

The general characteristics of $LiCoO_2$, $LiMn_2O_4$, lithium nickel oxide ($LiNiO_2$), and $LiFePO_4$ batteries, which are frequently used in EVs, are shown in Table 1 [25]. First developed by Sony in 1991, the $LiCoO_2$ battery has become the battery of choice for most personal electronic devices (tablets, cameras, laptops etc.) because of its long life, high energy density, and ease of manufacture [26]. This battery, which has good safety performance, has a practical capacity

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of 140-160 mAh/g, a theoretical capacity of 274 mAh/g, and an open-circuit voltage of 3.7 V [25]. Manganese oxide and nickel batteries have been introduced because the $LiCoO_2$ battery is more expensive than other batteries. As a result, manganese oxide batteries have become more suitable than nickel batteries [27]. Cobalt is expensive because it is available in limited quantities. Therefore, it may not be a suitable option for EV use. However, because of its high energy density, it is used in applications such as powering the Tesla Roadster and Smart Fortwo electric drive [28].

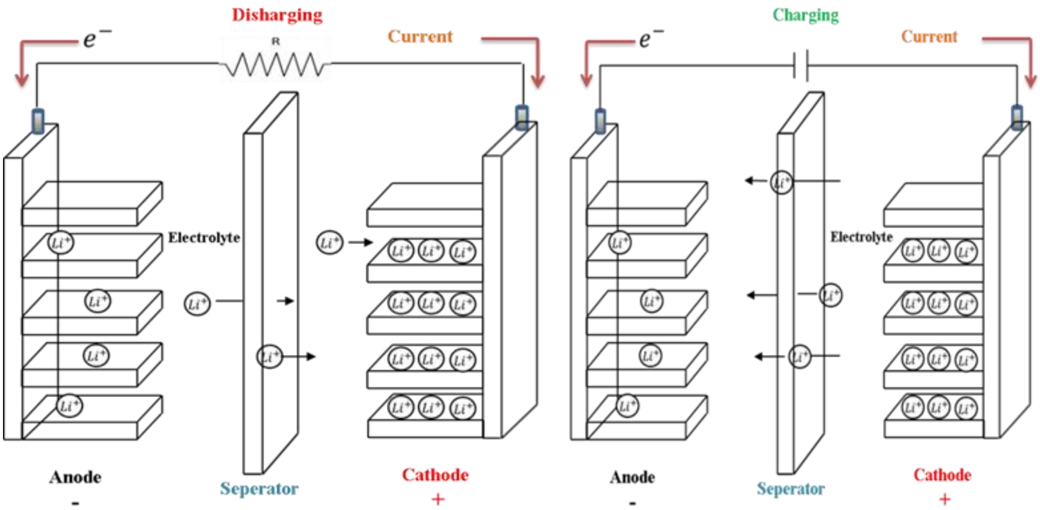

Fig. 2. Lithium-ion battery discharge and charging process

Table 1. Comparison of the characteristics of different lithium-ion batteries

Anode material	Theoretical Capacity (mAh/g)	Practical Capacity (mAh/g)	Open Circuit voltage (V)	Cost	Safety performance
$LiCoO_2$	274	140–160	3.7	high	fair
$LiMn_2O_4$	178	90–120	3-4	low	good
$LiNiO_2$	274	190–210	2.5–4.2	mid	poor
$LiFePO_4$	170	110–165	3.4	low	excellent

The theoretical capacity of the $LiMn_2O_4$ battery is 178 mAh/g, the open-circuit voltage is in the range of 3-4 V, and the practical capacity is 90-120 mAh/g. At the same time, these batteries have higher safety and lower cost, and their performance is higher than $LiCoO_2$ [25]. $LiMn_2O_4$ batteries are preferred in the market because of their high energy density, good safety performance, and low cost [29].

Lithium-nickel oxides (LNO, $LiNiO_2$) have been considered promising cathodes because of their positive properties, such as their inherent high energy densities and low material costs [30]. The theoretical capacity of the $LiNiO_2$ battery is 274 mAh/g, the practical capacity is 190-210 mAh/g, and the open-circuit voltage is 2.5–4.2 V. The disadvantages of this battery include harsh synthesis conditions and poor circulation stability [25]. In addition, the safety performance of these batteries needs to be improved.

$LiFePO_4$ battery has high discharge current and high power density. This battery has the lowest cost among lithium-ion batteries [31, 32]. This battery has a theoretical capacity of 170 mAh/g, a practical capacity of more than 110 mAh/g, an open-circuit voltage of 3.4 V, and good cycle performance [25]. In addition, it has an operating temperature of +60 °C to -30 °C [26].

3. Nickel-Based Batteries

Generally, the active material in nickel-based batteries is nickel hydroxide ($Ni(OH)_2$) as the positive electrode and potassium hydroxide (KOH) solution as the electrolyte. The negative electrode contains any metal iron-hydroxide, cadmium-hydroxide, or zinc-hydroxide ($Fe(OH)_2$-$Cd(OH)_2$ -$Zn(OH)_2$) material. At the time of discharge and charging ($Ni(OH)_2$) and Fe-Cd-$Zn(OH)_2$, metal (M) is formed [33]. Figure 3 shows the chemistry of the nickel-based battery during discharge and charging. Electrons released from the positive electrode move to the negative electrode with Cd and $(OH)_2$ [34]. As a result of this process, $Cd(OH)_2$ is formed. Since the reaction is reversible, the battery can be charged.

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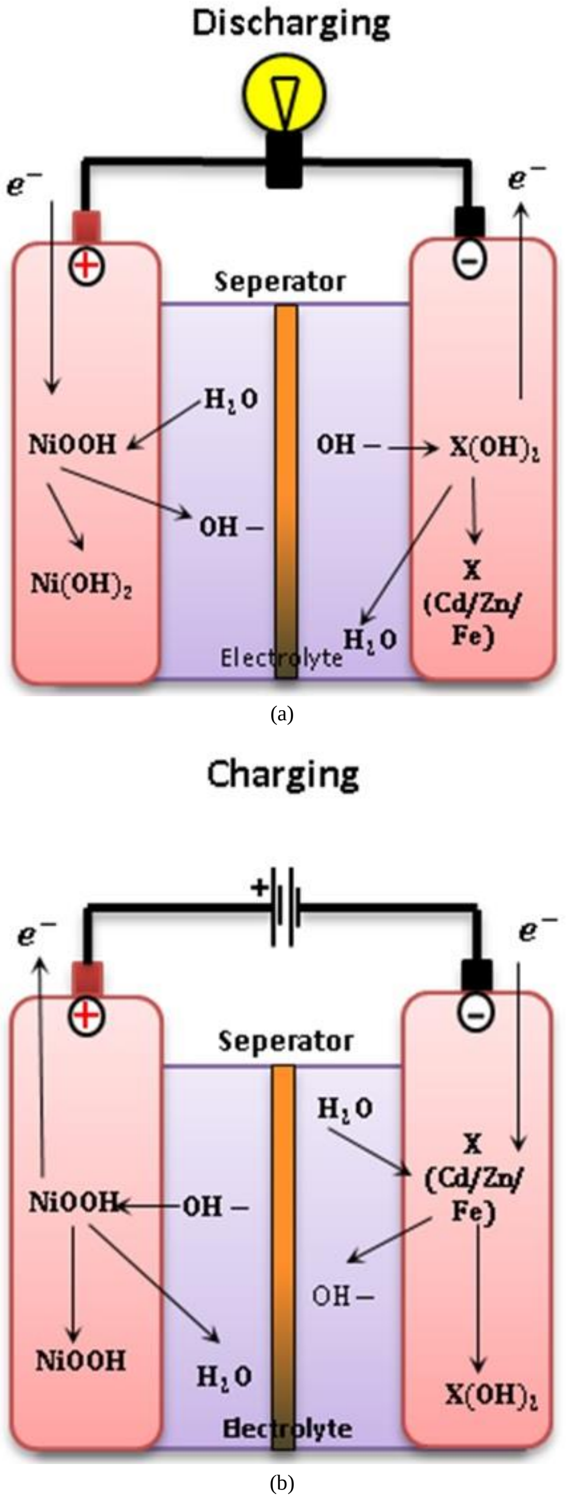

Fig. 3. Nickel-based battery chemistry. (a) during discharge (b) during charging

Nickel-Cadmium (Ni-Cd) batteries use KOH as the electrolyte, nickel oxide hydroxide NiO(OH) as the cathode, and metallic cadmium as the anode [35]. These batteries have a high charge/discharge rate. The total operating life varies between 8 and 25 years, depending on the operating conditions and battery design [36]. Ni-Cd battery technology has a cycle life of approximately 1500–3000 [37]. Ni-Cd batteries have been compared with LA batteries in terms of energy density, power density, and cycle life. As a result, it has a higher energy density by weight in the range of 55-80 Wh/kg and a higher specific power of 200 W/kg compared with LA batteries. It has also been found to have a longer cycle life [38].

The nominal voltage of this battery cell is 1.2 V. Battery discharge rate and battery temperature are important variables in chemical batteries. However, these parameters have little effect on Ni-Cd batteries compared with LA batteries. Therefore, Ni-Cd batteries can be used at high discharge rates without losing their nominal capacity. These batteries have a wide operating temperature range. A standard Ni-Cd battery cell can operate between -20 °C and +50 °C [39]. Berrada et al., stated that these batteries have high energy density, short response time, and high efficiency [40]. In addition, they stated that they have negative effects on the environment and that certain security controls should be provided. They also concluded that Ni-Cd batteries are more expensive than LA batteries ($600/kW).

Nickel-iron (Ni-Fe) batteries are resistant to overcharge and discharge current, as well as high temperature and vibration resistance. These batteries consist of an electrolyte potassium hydroxide, an anode made of iron, and a cathode made of oxide-hydroxide. Ni-Fe batteries are used in railway signaling, trucks/forklifts, and mines according to their properties. These batteries have lower performance at low temperatures and lower energy density (50 Wh/kg). In addition, these batteries have disadvantages such as approximately 40% discharge each month [41]. In addition, their costs are high. It is approximately four times more expensive than lead acid and lithium-ion batteries.

The positive electrode of nickel-zinc (Ni-Zn) batteries consists of nickel oxide and the negative electrode consists of zinc metal [42]. These batteries have an energy density of 70–110 Wh/kg [43]. Chau et al. found that the Ni-Zn battery (-39 °C to +81 °C) has a wide operating temperature range [33]. They also observed that Ni-Fe and Ni-Zn batteries are used less frequently in EV applications, although they have a wide operating temperature range. They stated that this is because of its low specific power, high cost, low life cycle, and high maintenance cost.

4. Metal-Air Batteries

Metal-air electrochemical cells consist of anode metal electrodes and oxygen cathode in the atmosphere [44, 45]. Li, Ca, Mg, Fe, Al, and Zn metals are used in the anodes of metal air batteries [46-49]. All metal-air batteries use thin gas permeable cathodes and alkaline water-based electrolytes such as potassium hydroxide. The metal electrodes most commonly used in such applications are zinc and aluminum. The maximum energy density of the aluminum-air (Al-air)

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battery is 220 Wh/kg, and that of the zinc-air (Zn-air) battery is 200 Wh/kg [50].

Lithium-air batteries (Li-air) are a more promising system than conventional batteries because of their higher theoretical specific energy densities [51]. These high specific energy density batteries can be used as a power source in EVs.

In Equation (4), the specific energy density of the anhydrous reaction of the Li-air battery is given [52]. The open circuit voltage (OCV) of this battery is 2.96 V, the energy density for the discharge condition is 3460 Wh/kg, and the specific energy density in the loaded state is 11,680 Wh/kg, excluding oxygen [51]. This is close to the energy density of gasoline (about 13,000 Wh/kg). At the same time, the energy density per unit mass and per unit volume of non-aqueous Li-air batteries is approximately 10 times and 6 times higher, respectively, than those of lithium-ion batteries containing a carbon anode and a $LiCoO_2$ cathode [51]. However, in addition to this advantage, the li-air battery has a high fire risk that may arise from the combination of air and humidity [44].

$$2Li + O_2 = Li_2O_2 \quad (1)$$

Mass production of metal-air batteries has not yet begun. However, it is predicted that it will have an important place in the electrochemical energy storage systems of the future [53]. However, the difficulties associated with the metal anodes, air cathodes, and electrolytes of these batteries need to be overcome in order to reach the abovementioned point.

5. Sodium-Beta Batteries

A sodium-sulphur (NaS) battery is a secondary battery that also uses a solid electrolyte that conducts molten sodium, molten sulphur/sodium sulphide, and ceramic sodium as active masses [54]. NaS batteries use a high-temperature reaction between sodium and sulphur, separated by a beta alumina electrolyte [35]. The use of a solid electrolyte in the NaS battery has resulted in it being unique among common secondary cells [45, 55]. It is a battery that can operate at high temperatures, such as 300°C, has 150–240 Wh/kg energy, and 150–230 W/kg power density [56, 57]. They also have high charge/discharge efficiency and a long cycle life.

NaS batteries have some drawbacks in terms of their use. These disadvantages include high cost, high daily self-discharge rate, and the need for high operating temperatures [35].

Sodium metal halide battery technologies have higher cell voltages than NaS batteries. Therefore, it has been used in EVs since the 1990s [44]. This type of battery is known as ZEBRA [31].

Sodium nickel chloride ($NaNiCl_2$) batteries are also called ZEBRA batteries. The active materials of the ZEBRA battery consist of porous nickel chloride ($NiCl_2$) as the cathode and liquid sodium as the anode. The electrolyte of these batteries consists of two parts [58]. The first is a ceramic electrolyte surrounding liquid sodium. The other is a secondary electrolyte consisting of sodium chloride ($NaCl_2$) and aluminum used for the cathode. The main feature of this battery is its high-temperature operation [31]. It also has a molten salt electrolyte that can be maintained in liquid form at a high temperature of 300-350°C. This battery also has high energy and power density, which makes it suitable for EV applications [59]. Where high power is required in EV applications, the operating temperature of the ZEBRA cell is typically around 300 °C [60]. However, the high operating temperature of this battery, around 300°C, requires the use of a battery construction that uses highly efficient thermal insulation and other temperature and corrosion resistant components, due to the need for durability and safety [61].

The $NaNiCl_2$ battery has a higher efficiency in the range of 90%, compared to Ni-Cd and Ni-MH [62]. EUROBAT focused on three batteries in its research [63]. These include advanced lead-based, lithium-ion and sodium chloride batteries. Improvements in these batteries will improve the affordability, reliability, and performance of HEVs or EVs.

In Equation (2) and Equation (3), the OCVs corresponding to normal cell reactions and metallic sodium are included in the case of using nickel and iron as transition metals. When Ni and Fe are used as transition metals as in Equation (5) and Equation (6), the theoretical specific energies are 788 Wh/kg and 729 Wh/kg, respectively [60]. At the same time, it was determined that these theoretical energy densities are about four times higher than the theoretical specific energy (161 Wh/kg) of the lead acid battery.

$$Ni + 2NaCI \leftrightarrow NiCl_2 + 2Na \quad (2)$$

OCV versus $Na/Na^+ = 2.58\ V\ (at\ 300°C)$

$$Fe + 2NaCI \leftrightarrow FeCl_2 + 2Na \quad (3)$$

OCV versus $Na/Na^+ = 2.33\ V\ (at\ 300°C)$

As mentioned earlier, the high operating temperature of $NaNiCl_2$ has strong demands for battery design, mechanical stability and safety, as well as thermal insulation, to be considered. Modern insulation technologies are used to minimize heat losses. However, there is permanent heat loss in this battery. Therefore, it is not considered a suitable solution for passenger cars for private use. However, it is seen as an acceptable solution for fleets with relatively high daily use, such as pure EVs and HEVs [64].

6. Fuel Cell

Interest in these batteries, which have high power density and zero emissions, is increasing [65, 66]. The fuel cell (FC) of these batteries consists of an electrolyte layer, which is in contact with an anode and a cathode on both sides [67].

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Figure 4 shows the operating principle of an FC. Here, fuel and air flow from the intake port to the fuel cell stack. Air and fuel inlets are made from separate places [11]. The anode is fed with a fuel such as hydrogen, and the cathode is fed with air [68].

During this process, (at the anode) hydrogen molecules are split into protons and electrons [11]. These generated positive particles reach the cathode tip via the electrolyte (which allows only positively charged particles to pass through) [69]. Electrons, which are negative ions at the anode tip, also tend to recombine with positively charged particles. This combination is provided by an external circuit, and positively charged particles move to the cathode side [70, 71]. Then, electrons passing to the cathode side combine with positively charged particles and oxygen to produce pure water and heat [72]. Electricity is produced as a result of the flow of electrons through this external circuit [73].

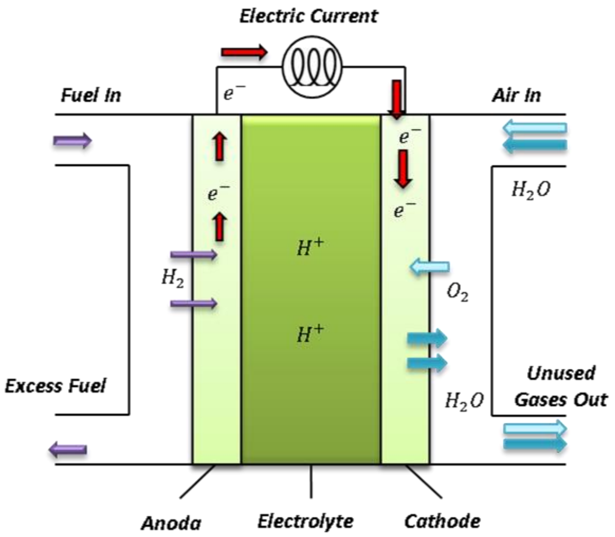

Fig. 4. Electrochemical reaction in the fuel cell (FUEL PELL STACK)

FCs have important features such as high efficiency and flexible power values [74-77]. Because of these features, it is mostly used in various vehicles such as passenger cars, light commercial vehicles, busses, and trucks.

A full FC EV fuel tank consists of an FC stack, DC-DC power converter, inverter, and electric motor [78]. Figure 5 shows the EV topology with the battery-FC. According to this topology, there is also a small battery in the system. In the functional process of the hybrid system with FC-battery, battery-powered start-up is ensured, preventing the FC from operating in the low-efficiency areas. In addition, the high current required to run the electric motor is provided by this battery [79]. After the vehicle is started, FC comes into play when necessary, both providing energy to the electric motor and charging the battery [80].

To store hydrogen, a hydrogen storage system must be used in the car. A solution has been selected by almost all original equipment manufacturers (OEMs). This solution is a type IV compound (metal or plastic cylinder wrapped in carbon fiber) storage system for gaseous hydrogen with a storage pressure of 700 bar. The pressure cylinders of this system are composed of valves, sensors, and pipes [81].

The technical challenges associated with the FCHEV are also reviewed in the studies. Components must be fully integrated into the systems. There are obstacles to the successful implementation of the hydrogen fuel infrastructure that can be addressed. At the same time, heavy-duty hydrogen trucks such as long-haul trucks are expected to be introduced if the demand for FCEV increases. It will require heavy-duty trucks and numerous stations compared with light-duty needs. The Department of Energy (DOE) develops and tests complete system solutions that validate integrated hydrogen and fuel cell technologies for transportation, infrastructure, and power generation in a system context under current world operating conditions [82].

With the rise of EVs, charging requirements will increase at the same rate. Therefore, a strong station network is required for both consumers and fleets [83]. Various options are available for the electric vehicle (EV) charging infrastructure. Therefore, a versatile infrastructure procurement process is required. Setting up charging infrastructure involves infrastructure considerations such as cost, regulations, safety, efficiency, layout, and equipment type. This charging infrastructure can also include complex payment structures, data collection, ownership models, and parking and signage requirements [84].

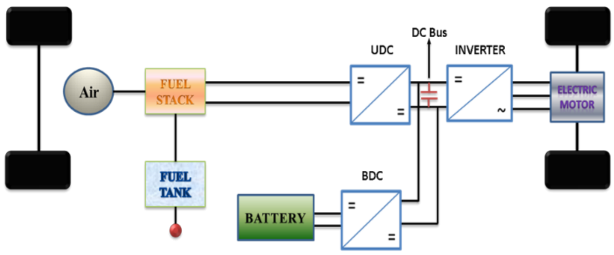

Fig. 5. Topology of fuel cell electric vehicle

7. Conclusion

Because of the research, it was determined that more than 70% of the emissions of the transportation sector belong to road transport. EVs and HEVs, on the other hand, are promising sources of reducing noise pollution, fuel consumption, and environmental pollution. Because of the studies carried out in this context, it has been seen that the European Union has supported the studies to have more than 80% EVs compared to the total vehicles by 2030.

It has been seen that the rapid spread of EVs and HEVs in society has brought some demands. High-range, suitable, and reliable vehicle demand can be given as an example. For this

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reason, it has been determined that research should focus on battery technology, which affects the range and performance of EVs and HEVs and is the most expensive part. In studies conducted in this context, it has been determined that ESS has several disadvantages, such as low power density, battery life, and high cost. It has been clearly seen that these disadvantages have guided the studies.

Batteries in EV technology, which is one of the important studies today, are examined according to many parameters such as long life, high energy density, high life cycle, high power density, low cost, and operating temperature range. Comparisons are made with other ESSs according to these parameters, and as a result, an appropriate ESS is preferred for EVs and HEVs. When the studies carried out in line with these criteria are analysed, since lithium-ion batteries have a high energy density, they are used in many applications such as HEVs and EVs. However, lithium batteries, which are classified according to their cathode materials, have some advantages and disadvantages. For example, it was concluded that $LiCoO_2$ batteries are more expensive due to the cobalt material and are not suitable for use in EVs. For this reason, it has been seen that $LiMn_2O_4$ battery with high energy density, lower cost, and higher reliability than $LiCoO_2$ are preferred as an alternative in the market. As an alternative, it has been determined that studies on lithium-nickel oxide (LNO, $LiNiO_2$) batteries have been conducted. It has been observed that promising results have been obtained because of its positive properties such as low material costs and natural high energy densities.

In this study, different types of batteries were analysed, especially for EVs and HEVs. In the analysis, the life cycles, energy and power densities, efficiency, operating temperature ranges, service life, and costs of the batteries were taken as the basis. In terms of cost, Ni-Cd batteries were found to be $600/kW more expensive than lead-acid batteries. Therefore, it has been determined that lead acid batteries for HEVs and EVs are preferable in terms of cost.

It has been observed that the $NaNiCl_2$ battery used in HEVs and EVs has a higher efficiency of 90% compared with Ni-Cd and Ni-MH. At the same time, $NaNiCl_2$ battery has been found to have high energy and power density in EV applications. In addition, $NaNiCl_2$ batteries have higher performance than lead-acid batteries. Other nickel-based Ni-Fe and Ni-Zn batteries have been observed to have a wide operating temperature range. However, they have disadvantages such as low specific power, high cost, low life cycle, and high maintenance costs. Because of these disadvantages, it has been observed that they are less used in EV applications.

Metal-air batteries technology and Li-air batteries have been seen to come to the fore with their high energy densities. when a solution is found for the negative properties of these batteries, it can contribute to solving the range problem, gaining EV and HEV's trust in the society, and increasing the affordability of EVs and HEVs accordingly.

FCs, which are in the electrochemical energy storage group, have important features such as high efficiency and flexible power values. Because of these advantages, they are mostly used in various vehicles such as passenger cars, light commercial vehicles, busses, and trucks. Battery types in development are still in the research phase. For EVs to be more advantageous and preferable than traditional vehicles, this battery technology needs to be further developed. Once this development reaches a certain level, the demand for EAs will increase further.

Authorship contribution statement for Contributor Roles Taxonomy

Zeyneb Nuriye Kurtulmuş: Regarding the issue raised in the article, the writing process of the article included the application of data collection, relevant data solution determination of methods, and solution methods. **Abdulhakim Karakaya:** He contributed to the implementation of the techniques and analysis of the findings.

Conflict of interest

There are no conflicts of interest in this study.

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