

EVOLVEMENT OF BATTERIES OF ELECTRIC VEHICLES

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ABSTRACT

The review article describes the basic concepts of energy storage systems in hybrid electric vehicles and Electric vehicles. . Various Energy Storage System (ESS) topologies including hybrid combination technologies such as hybrid electric vehicle (HEV), plug-in HEV (PHEV) and many more have been discussed. The main focus of this paper is evolvement of batteries used in electric vehicles and to make them more cost effective, environment friendly. These technologies based on different combination of materials used in the place of cathodes. Different battery storage parameters and technical terms stated. Furthermore the raw materials used for modern batteries and its demand and ability to feed market have been stated.

Keywords: Analysis, Investigation, Research.

I. INTRODUCTION

Animal Electricity?

The modern incarnation of electrochemical battery is credited to the Italian scientist Alessandro Volta who put together the first battery in response to the misguide findings of his college Luigi Galvani. In 1780 Galvani had shown the legs of frogs hanging on brass hooks would twitch when touched with a probe made from a dissimilar metal he believed that this is caused by electricity from within the frogs tissues and called it animal electricity.

Voltaic pile

Volta suspected that the electric current came from the two dissimilar metals and it was being transmitted through the frogs tissues not originated from it. He experimented with stacks of alternating plates of silver and Zink separated by cloth soaked in salt water and found that an electric current did in fact flow through the wire applied to both ends of the pile. Volta had developed the first electrochemical battery called **Voltaic pile**, each pair of silver and Zink form the electrode of voltaic or galvanic cell.

The Zink plate would react with the salt water producing an accumulation of electron an electrode that results in the production of electron is known as an **anode**, meanwhile at silver plate simultaneous reaction with the salt water occurred enable it to accept electrons this is known as a **cathode**. The chemical that both the electrodes react with in this case salt water is known as an **electrolyte**. The electrolyte also functions for the pathway for the transfer of positively charged ions to balance the flow of electrons from the anode to cathode keeping the reaction running. in order to prevent the ions of the more Nobel meal from plating out the other electrode. a **semi permeable membrane** is sometimes used to divide the reaction halves within the electrolyte this type of chemical reaction is known as **reduction Oxidation reaction** or Redox reaction. The entire reaction can be split into two half reactions and in the case of an electrochemical cell one half reaction occurs at the anode while the other at the cathode. Each of these reactions possesses a particular standard potential or relative ability to either produce or absorb electrons. The difference in standard potentials between the electrodes become the cells overall **electrochemical potential** or its **voltage**. The greater this differences the greater electrochemical potential and the higher the cells voltage.

Individual cells can be combined in two configurations that can both increase the total voltage and current capacity; this is known as a **battery**. On primary batteries the electrodes become depleted as they release their positive or negative ions into the electrolyte or they buildup the reaction products on the electrodes prevent the reaction from the continuing this results in a **one-time use battery**.

In secondary batteries the chemical reaction that occurred during the discharge can be reversed however the process is not perfect as each charge cycle cause the battery to loose performance over time. With each battery chemistry having its own particular mechanism of weird, this is exacerbated when a battery discharged and recharged in highly frequent manner, beyond the advent of the voltaic pile batteries took on more practical forms with various configurations and chemistries being developed thereafter however all our primary batteries would be permanently drained when the chemical reactions were spent.

Electric Vehicles

In the early 1990's the California Air resources board or carb began a push for more fuel efficient lower emissions vehicle with the ultimate goal of transitioning to zero emission vehicles. This initiative intersected with the recent refinement of nickel metal hydride battery technology making practical electric vehicles a viable commercial option to pursue. By the late 1990s mass-market electric vehicle production had started once again taking a more risk adverse approach many automakers started to develop all electric models based on existing platforms in their model lineup. Some notable all electric vehicles were the Toyota RAV EV Honda EV + hatchback, Ford Ranger EV, S10 EV pickup. Everyone while other battery chemistry's were explored these first generation modern electric vehicles all predominantly used nickel metal hydride batteries in their power trains due to the limitations of the vehicle size and target price point most of these vehicle employed battery pack sizes of around 30 Kilowatt hours. This was sufficient enough to allow these early vehicles to operate at highway speeds comfortably with range of around 160 km or about a hundred miles for the first time electric vehicles were now a practical option for use outside of cities making all electric suburban commuting possible. While these early vehicles proved to be popular in niche such as short distance urban use and fleet vehicles they still lacked mass market due to their image of being slow, low powered, expensive and range limited. In the US lower gas prices and higher profit margins left them mostly ignored in favor of larger truck based vehicles. It would take further advancement for them to even be seems as a competitive product by the automotive market.

II. METHODOLOGY

Important parameters in battery Storage

Specific Energy (Wh/kg): it is the amount of energy can be store per mass unit.

Energy density (Wh/L): It specifies the amount of energy store per unit of volume.

Specific power (W/kg): It quantifies how much power it can generate per unit mass.

Other parameters that determine battery suitability for an application include its self-discharge rate typically measured in % of charge loss per month, its charge recharge cycle durability, charge recharge energy efficiency, nominal cell voltage and cost per unit of energy.

Lead Acid Battery

In 1859 the French physicist Gaston plant would advent the lead acid battery. The first ever battery that could be recharged. A lead acid cell consists of lead anode and a lead dioxide cathode immersed in sulfuric acid electrolyte. While discharging both electrode react with the sulfuric acid produce lead sulphate while the electrolyte loses its dissolved sulphuric acid, but what made this discovery so important was that these chemical reactions could be reversed by passing revers current through the battery recharging it.

By 1880s lead acid battery would take on more practical form with each cell consisting of interlaced plates of lead and dioxide this mutilate design made lead acid batteries far easier to mass produce as well as allow the cells to be stacked easily for different application requirements. Because the electrodes and electrolytes within a battery aren't 100% conductive, they all inherently have internal resistance. Lead acid batteries by nature have low internal resistance making them ideal for producing large surge of current, This property made them ideal for powering large current intensives loads such as electric motors,

By the end of 1880s the lead acid batteries brought about the rise of the first electric vehicles in Europe, before the proliferation of the internal combustion engine electric automobiles held many speeds and distance records among the most notable of these records were the breaking of the 100 Kilometer per hour speed barrier by Camille Nausea on April 29th 1889 in his rocket shaped vehicle in Jamaican tongue.

Nickel Hydrogen Battery

The most famous vehicle to date the lunar lander made its first drive on the moon 1971 though it helped to raise the profile of electric vehicles from a technical standpoint it operated on to silver oxide primary batteries offering little in crossover technology to its terrestrial counterpart. Fundamentally little has changed in battery technology since the first Golden age of electric vehicles still limiting their speed and range to nom competitive levels.

In the late 1960's research has begun by the globe communications company 'Compsat' on a relatively new battery chemistry called **nickel hydrogen** designed specifically for use on satellites probes and other space

vehicles. These batteries used hydrogen stored at up to 82 bar with nickel oxide hydroxide cathode and a platinum based catalyst anode that behaves similar to a hydrogen fuel cell. The electrolyte used was alkaline chemical potassium hydroxide as the battery discharges the hydrogen is consumed by the anode producing water which is simultaneously consume the nickel electrodes of reaction. the pressure of the hydrogen would decrease as the cell is depleted offering a reliable indicator of the batteries charge though nickel hydrogen batteries offered only a slightly better energy stored capacity than lead acid batteries. Their service life is exceeded 15 years and they had a cycle durability exceeding 20,000 charged recharge cycles they were also very resilient over charging and overheating. by the early 1980's their use on space vehicles became common appearing on several notable mission such a the mercury messenger, mars Global surveyor, the Hubble space telescope even the international space station.

Nickel cadmium cells

Nickel hydrogen sulk emissary was based on nickel cadmium, one of the first rechargeable alkaline cell chemistry's ever developed first created by Voldemort younger of Sweden. In 1899 nickel cadmium cells also used nickel oxide hydroxide cathode with a potassium hydroxide electrolyte though they used the toxic heavy metal cadmium as an anode though this offered slightly better energy density and specific power than lead acid cells. they offered almost six times the cycle durability making them ideal for consumer products use. Rechargeable Nickel cadmium batteries could be found powering early portable power tools photography equipment flashlights emergency lighting toys and portable electronic devices there are higher cost and lackluster energy capacity as well as there are relatively more complex charging requirement make them less than ideal for electric vehicle use,

They also suffer from memory effect a condition in which a battery gradually loses a maximum engine capacity if they repeatedly recharged after being only partially discharged as work was being done on nickel hydrogen batteries. Simultaneously a less bulky method for storing hydrogen was being explored at the battery Geneva research center known as nickel metal hydrides this new chemistry relied on metal hydrides a class of materials containing metal or bonded to hydrogen to function as an anode over the next two decades. researchers research into metal hydride cell technology was supported heavily by both Daimler-Benz and by Volkswagen Howie group resulting in the first generation of the batteries achieving some capacities similar to nickel hydrogen though with a fivefold increase in specific power however these suffered from electrode alloys instability within the alkaline electrolyte and consequently suffered from low charged cycle durability typically around 500 cycles finally.

Finally in 1987 a breakthrough in research led on anode material composed of a mixture of lanthanum, neodymium, nickel, cobalt and silicon that allowed the cell to retain 84% of its charge capacity after 4000 charge recharge cycles. This breakthrough led to the first consumer grade nickel metal hydride batteries to become commercially available in 1989.

Nickel metal hydride batteries

By the late 1990 more advanced alloys consisting of titanium and nickel modified with chromium cobalt and manganese would result in specific energies almost two and half times higher than that of lead acid cells. These new anode materials also offers energy densities five and half times greater and with their already drastically improved specific power for first time in automotive history. A battery technology had emerged as a viable successor to the lead acid battery. Nickel metal hydride batteries did suffer some drawbacks such as higher self-discharge rate than lead acid batteries memory effect issues and costs as a high as two to three times more per kilowatt hour when compared to lead acid battery though the emergence of inexpensive embedded microprocessors advanced charging and battery monitor techniques could mitigate many of these chemistry issues.

Nickel metal hydride become widely popular in the consumer space quickly replacing nickel cadmium and enabling a new surge in high consumption mobile electronic. Ultra-low self-discharge variant would eventually be developed in 2005, for the consumer market further increasing their appeal almost 100 years after the first golden age of electric vehicles. A confluence of several factors reignited interest in electric vehicles once again.

III. MODELING AND ANALYSIS

Lithium Ion Batteries

During 1970's just after the peak of the energy crisis in an attempt to challenge Bell Labs and its image of innovation ExxonMobil began to back a breakthrough made by English chemist Stanley Wittingham. He discovered a way to make an electrode from a layer material that could store lithium ions within sheets of titanium sulfide. The lithium ions could move from one electrode to the other creating a battery from the highly reactive properties of lithium itself. In lithium based cells the electrolyte does not take parts in the reaction but rather mediate the movement of ions controlling the cells characteristics. The method developed by Wittingham was known as intercalation and it permitted the addition of lithium ions into a host material without significantly changing its structure, because metallic lithium was used as the anode. The first variants of lithium based batteries were known as lithium metal batteries, compared to other batteries chemistry's they have incredibly high energy densities with some high as ten times that of lead acid cells. They also have self-discharge rates well below 1% per month as well as long shelf life easily surpassing a decade. Wittingham's initial use of titanium disulfide had proven to be impractical its raw form cost over \$1000 per kilogram in the 1970s and it also required a complex and costly synthesis process. Furthermore when exposed to air titanium disulfide reacts to form hydrogen sulfide compounds which an unpleasant odor are toxic to most animals. The experimental cells were dangerous as pure lithium will instantly react with water or even moisture in the air releasing flammable hydrogen gas. By the late 1970s newer cathode materials would result in the first consumer lithium metal primary batteries, these tend to be found in low power consumer electronic medical devices and on computer equipment where a long life and high densities are needed. Most of these new lithium cells found in consumer applications used Manganese dioxide as a cathode with a salt of lithium dissolved in an organic solvent as an electrolyte. Despite the advantages offered by lithium a practical rechargeable lithium ion batteries still remained a challenge, the electrochemical reaction that enabled lithium cells to function so effectively also made them prone to ignition when overcharged the cathode would also quickly corrode from repeated charge and discharge cycles.

The problems of Wittingham's lithium cell would soon be solved by American material scientist and solid state physicist John B Goodenough had become very familiar with a family of compounds known as metal oxides. These compounds combined oxygen and a variety of metal elements. He proposed that metal oxides would allow for charging and discharging at higher voltage than Wittingham cells which would result in both greater energy storage as well as volatility. Steam experiments with several metal oxides and had concluded cobalt was the most stable allowing lithium ions to be extracted at up to 4 volts without eroding the electrodes. Completed in 1980 the lithium cobalt oxide cathode based lithium-ion cell became a massive breakthrough. The world's first rechargeable lithium ion battery had an energy density unmatched by anything else yet seen offering a specific energy and an energy density almost seven times that of lead acid battery because lithium cobalt oxide was such a stable positive electrode material could be used with a negative electrode material other than lithium metal.

In that same year Moroccan engineer Rasheed Sami demonstrated the reversible electrochemical intercalation of lithium in graphite inventing the far safer and more stable lithium graphite anode eliminating the need for pure metallic lithium. During recharging. When a voltage is applied the positively charged lithium ions from the cathode migrate to the graphite anode and become lithium metal because lithium has a strong electrochemical driving force to be oxidized upon discharging. It migrates back to the cathode becoming a positive lithium ion again while giving up its electron to the cobalt. In 1991 Sony combined Goodenough's cathode and a carbon anode into the world's first commercial rechargeable lithium ion battery. The results were a huge commercial success not only in battery cells but also via the abundance of consumer electronic products that could now be produced. The lithium ion battery solved one of the Sony's biggest technical obstacles, powering its leading electronics product handled video cameras making them a huge seller.

Lithium Cobalt Oxide

Though lithium cobalt oxide cells have a high capacity, their more reactive nature made them susceptible to thermal runaway when overcharged or physically damaged. This susceptibility to explosion fire made them unsuitable for large capacity mobile use.

Lithium ion cathode based lithium iron and phosphate

By late 1990s 'goodnough' once again made a huge leap in battery technology by introducing a far more stable lithium ion cathode based lithium iron and phosphate. This cathode material was thermally stable. It allowed the formation of crystal and lithium ferro phosphate structures that permitted ions more pathways to move in and out of the material. These classes of cathodes called phosphate lines possess a similar structure as mineral outline. A magnesium iron silicate that is a primary component earth's upper mantle lithium fare phosphates came as the successor to a similar group of cathodes made from magnesium which also utilized a crystal structure to improve their most ability. While effective they suffer from poor cycling stability due to the tendency of manganese to dissolve in the electrolyte they also weren't as thermally stable as lithium ferro-phosphates though they were cheaper to construct to relative low cost manganese. Lithium ion cells can now be made safely into large formats that could undergo rapid charge discharge cycles. This new cathode material finally opened up lithium ion batteries to new high demand applications from power tools to hybrid and electric vehicles.

In 1997 at the Los Angeles international Auto show Nissan introduced the ultra EV aside from its peculiar design that fused a sedan with a minivan. It possessed another unique characteristic it was the first commercial electric vehicle to use lithium ion batteries in its power tree though it only sold 200 units primarily. For fleet us its 33 Kilowatt hour battery pack which weighed 360 kilograms or around 800 pounds could power comfortably to a range of around 200 Km or about 125 miles. Despite lithium-ion batteries becoming a viable option for electric cars the second half of the 1990s into the mid-2000s were primarily dominated by the more risk-averse technology of hybrid powered vehicles.

(The Modern EVs)And even these successful early models such as the Toyota prius and the Honda insights were generally powered by nickel metal hydride technology. The time lithium ion batteries were still relatively improving for vehicle use and also cost more per Kilowatt hour it would take a small Silicon Valley startup. Tesla motors starting with their announcement of producing a luxury electric sport car that could go more than 200 miles on a single charge to ignite momentum for the broader consumer appeal of electric vehicles by 2010 Tesla would grow to establish a manufacturing facility in California winning wide acclaim for its cars and becoming the largest auto industry employer in California. Their success spurred many larger automakers to accelerate work on their own electric vehicles by 2020. Virtually, every major manufacturer has some form of all-electric vehicle offering among the product line, the vast majority achieve ranges between 160km to 320km or 100to 200 miles. With recharge times from 4 to 8 hours some more advanced models such as tesla sl lonh range model 3 can over match or exceed the range of gasoline engine achieving over 600 kms or 380 miles.

Lithium nickel manganese Cobalt oxide cathode (NMC)

Around 2010 the cathode material of lithium ion cells would once again evolve with advent of lithium nickel manganese Cobalt oxide cathode or NMC. NMC cells also have the lowest rate of the different types of lithium ion cells. They are currently in high demand and have been used by almost every major electric vehicle manufacturer. Curiously Tesla is known for being the only manufacture, which does not use NMC cell technology but rather much older lithium nickel cobalt aluminum oxide cathode or NCA. NCA cells have been around since 1999 for special applications it shares similarities with NFC by offering high specific energy. and specific power with a longer lifespan however NCEA batteries are not as safe requiring special safety monitoring measures to be employed for use of vehicles Tesla claims that using them is more cost effective due to lower cobalt content.

IV. RESULTS AND DISCUSSION

Comparison of alkaline batteries and Lead Acid batteries

A typical modern double alkaline primary battery for an example when compared to lead acid cell has almost 4 & half times the specific energy, 5 & half times the energy density but only one-third the specific power. They also have incredibly low self-discharge rates losing only about 0.17% per month as opposed to the 3 to 20% for lead acid cell. Where lead acid batteries stand out compared to other more superior chemistries is in costs a lead acid battery can store almost 40 times more energy per dollar than the more energy dense double a battery.

Over the next 60 years electric vehicles entered a dark period with little advancement in technology cheap abundant gasoline and continued improvements of the internal combustion engine hampered demand for Electric vehicle and alternative fuel vehicle, however, in US during the early 1970's soaring oil prices and gasoline shortages peaked some interests in EV once again. Though the enthusiasm was short lived the initiative did the yield some research and development as well as a few experimental fleet vehicle programs it should be noted that it was doing this period in history.

Primary Batteries

Primary battery	Cathode material	Anode material	Electrolyte/reaction	Nominal voltage /current	Practical capacity
Zinc-carbon and alkaline manganese	MnO ₂	Zn	Aqueous KOH/NH ₄ Cl Zn + 2MnO ₂ + 2H ₂ O → 2MnOOH + Zn (OH) ₂ Zn + 2MnO ₂ → ZnO + Mn ₂ O ₃	0.16–44 A	75–35 A·h/kg
Zinc-air	O ₂	Zn	Alkaline electrolyte Zn + 2OH ⁻ → Zn (OH) ₂ + 2e ⁻ (anode) O ₂ + 2H ₂ O + 4e ⁻ → 4OH ⁻ (cathode) Zn + 1/2 O ₂ → ZnO (overall reaction)	0.4–2 mA	40–600 mA·h
Silver-oxide	Zn	Ag ₂ O	KOH or NaOH aqueous electrolyte Zn + Ag ₂ O → ZnO + 2Ag (overall reaction)	1.5–1.6 V	165 mA·h
Lithium-sulfur dioxide	Teflon-bonded acetylene black	Li	2Li + 2SO ₂ → Li ₂ S ₂ O ₄ (overall reaction)	2.7–2.9 V	~260 W·h/kg
Lithium-thionyl chloride	Porous carbon	Li	4Li + 2SOCl ₂ → 4LiCl + S + SO ₂ (overall reaction)		450–600 W·h/kg
Lithium-manganese dioxide	MnO ₂	Li	Ion conducting organics Li → Li ⁺ + e ⁻ (anode) 2MnO ₂ + Li ⁺ + e ⁻ → MnO ₂ ⁻ (Li ⁺) (cathode) MnO ₂ + Li → MnO ₂ ⁻ (Li ⁺) (overall reaction)	3.60 V	200 W·h/kg
Lithium-carbon monofluoride	Polycarbon fluoride	Li	xLi + CFx → xLiF + xC (overall reaction)	2.8 V	200–600 W·h/kg

Figure 1: Primary Batteries

Secondary Batteries

Secondary batteries	Cathode material	Anode material	Electrolyte/reaction	Nominal voltage (V)	Practical capacity (W·h/kg)
Lead-acid	PbO ₂	Pb	H ₂ SO ₄ aqueous solution Pb + SO ₄ ²⁻ ↔ PbSO ₄ + 2e ⁻ (anode) PbO ₂ + 4H ⁺ + SO ₄ ²⁻ + 2e ⁻ ↔ PbSO ₄ + 2H ₂ O (cathode) PbO ₂ + 2PbSO ₄ + Pb ↔ PbSO ₄ + 2H ₂ O (total reaction)	2	30–50
Nickel-cadmium	NiOOH	Cd	KOH aqueous solution Cd + 2OH ⁻ → Cd(OH) ₂ + 2e ⁻ (anode) 2NiOOH + 2H ₂ O + 2e ⁻ ↔ 2Ni(OH) ₂ + 2OH ⁻ (cathode) 2NiOOH + Cd + 2H ₂ O → Ni(OH) ₂ + Cd(OH) ₂ (total reaction)	1.2	50
Nickel-metal hydride	NiOOH	Hydrogen adsorbed alloy	KOH aqueous solution H ₂ + 2OH ⁻ ↔ 2H ₂ O + 2e ⁻ (anode) 2NiOOH + 2H ₂ O + 2e ⁻ ↔ 2Ni(OH) ₂ + 2OH ⁻ (cathode) 2NiOOH + H ₂ ↔ 2Ni(OH) ₂ (total reaction)	1.2	100
Lithium-ion	LiCoO ₂	C + Li/Li	Organic electrolyte with lithium salt Li (C) ↔ Li _{(1-x)}} (C) + xLi ⁺ + xe ⁻ (anode) xLi ⁺ + xe ⁻ + Li _{(1-x)}} CoO ₂ ↔ LiCoO ₂ (cathode) Li (C) + Li _{(1-x)}} CoO ₂ ↔ LiCoO ₂ (total reaction)	3.6	150–200
Lithium-sulfur	S	Li	Liquid electrolyte Li ₂ S ₈ + 2e ⁻ + 2Li ⁺ ↔ 2Li ₂ S ₄ Li ₂ S ₄ + 2e ⁻ + 2Li ⁺ ↔ 2Li ₂ S ₂ Li ₂ S ₂ + 2e ⁻ + 2Li ⁺ ↔ 2Li ₂ S	2.15	2600–2800
Lithium-air	LiCoO ₂	C	Liquid or gel electrolyte 2Li + O ₂ ↔ Li ₂ O ₂ 4Li + 6H ₂ O + O ₂ ↔ 4(LiOH·H ₂ O)	3.1	3620–5200

Figure 2: Secondary Batteries

V. CONCLUSION

The End of Electric Vehicle Era (1910)

In the early 1900's the electric vehicle began to grow popularity in the US after thriving in Europe over 15 years by 1905 in Us 40% of automobiles were power steamed, 38 % by electricity and only 22% by gasoline however the first golden age of electric vehicles would soon end as gasoline vehicles to travel further and at higher speeds. Lack of sufficient electric infrastructure for recharging batteries would also hinder adoption, Henry Ford's mass produces Model T was the final blow to the electric car introduced in 1908 the model T made gasoline power cars widely available and affordable.

by 1910 a gasoline powered car could be purchased for as low as 650\$ this was less than half of the cost of many electric vehicles at that time within few years most electric vehicles manufacturers ceased production

most early electric vehicle had top speed well below 30km/h or about 18 miles per hour and generally had a range of about 40km or about 24 miles at best.

Despite these limitations Lead acid battery still remain a part of modern automotive industry as their high current capacity made them ideal for powering electric starters in gasoline and diesel engines. Making their first production appearance on several Cadillac vehicles in 1912 the lead acid battery would evolve with vehicle design over the next century becoming a key part of the electromechanically and electronic system. Particularly on heavily computerized vehicles of today even 150 years later the lead acid batteries still retains the significant market share due to lack of any cost effective alternatives. For internal combustion powered vehicles electric systems and other durable short cycled high demand use cases the energy storage characteristics of battery chemistry can be compared with handful key primes.

Electric Vehicles Today

In 1997 at the Los Angeles international Auto show Nissan introduced the ultra EV aside from its peculiar design that fused a sedan with a minivan. It possessed another unique characteristic it was the first commercial electric vehicle to use lithium ion batteries in its power tree though it only sold 200 units primarily. For fleet us its 33 Kilowatt hour battery pack which weighed 360 kilograms or around 800 pounds could power comfortably to a range of around 200 Km or about 125 mils. Despite lithium-ion batteries becoming a viable option for electric cars the second half of the 1990s into the mid-2000s were primarily dominated by the more risk-averse technology of hybrid powered vehicles.

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