

Title
NANO CATALYTIC COATING METHOD USED IN GAS ELECTRODES

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ABSTRACT

The need to coat a current collector with catalytic powders has been a long-standing challenge to anyone in the fuel cell, water electrolysis and cellulose digestion fields among others. This paper gives detailed directions as how to produce a very highly active electrochemical surface for electrodes used in batteries, fuel cells and electrolysis apparatuses among other applications.

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1. Introduction:

To imbed particles with a plated surface is well known in many aspects of mechanical engineering. Two examples are to nickel plate a saw blade while suspending diamonds within the electrolyte to produce a ceramic-cutting blade. In that case, the nickel is allowed to remain over the particles, and at first use, this surface is physically removed. Another example is to fill the plating heavily with a metallic powder to increase the physical strength of the resulting compounded sheet.

We loaded nickel plating with nano catalysts in a way that left them firmly adhered to all surfaces of a nickel foam current collector while stripping the plating off of the powder surfaces resulting in a highly catalytic current collector with almost no resistance to the catalytic powders. We used nano-sized powders for even higher catalytic activity. The objective was to produce highly efficient water electrolysis electrodes.

This paper gives the details from patent application US-2011-0114496-A1 herein so anyone can use this unique and powerful coating technique for water electrolysis and other electrochemical application.

This work was accomplished between Feb 2010 to May 2012 at DoppStein Enterprises laboratory in Marietta, GA USA.

2. Background

The techniques to add a catalyst to a nickel current collector for electrolysis is often slow and energy consuming such as Raney Nickel (or similar) applications, sputtering or using thermal flow characteristics of other metals such as silver to act as an adhesive. All of these have serious problems when scaled up for large volume hydrogen production, are energy expensive to make and/or are not robust enough to withstand the rigors of an electrolyzer.

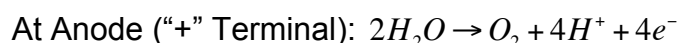
The method detailed below results in the nickel foam surface being fully coated on all intricate surfaces within the foam, thus providing a solid-state 3D reaction surface much like a fluidized bed reactor that is frozen in space.

3. Principles of Electroplating

The chemical reaction for acidic nickel electroplating is shown below assuming a nickel counter electrode and the acidic "Watt's" bright nickel electrolyte. We used a nickel foam cathode, but many metals plate well with nickel.



If the voltage is too great, then water electrolysis also occurs with hydrogen bubbling from the cathode (AKA Working Electrode) and oxygen from the anode (counter electrode) by the equations:



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The resulting gas bubbling is undesirable both for possible pitting of the nickel plating and as a bypass of current causing poor efficiency of the nickel plating. So the voltage should be held just below the level that causes gassing.

The amount of nickel deposited follows Faradaic principles where 1 gram equivalent of a metal has a value of 96,487 coulombs (ASec). Notice that Faraday demonstrated pragmatically (by inventing the ammeter) in the early 1800's, that matter and energy are equatable. This is known as Faraday's Constant. Using this constant and knowing that nickel's atomic weight is 58.71 and has a valence of 2, the weight of nickel deposited at the cathode and the amount dissolved from the anode can be calculated to be:

$$\text{Grams} = (\text{Ahr} / 96487 / 2) * 58.71 \text{gaw}$$

$$\text{Grams} = \text{Ahr} * 1.095$$

Therefore, 1 ampere-hour will deposit (or dissolve) 1.095 grams of nickel assuming that all the current is going to electroplating and none to water electrolysis.

4. **Plating Process step-by-step:**

4.1 **Use porous nickel current collector**

- Source INCO
- Density: 1450 g/m²
- Pore size: 590 um
- Thickness: 1.4 mm

4.2 **Electro-Cleaning to remove any organic residue on nickel foam**

- 5% Sodium Hydroxide (NaOH)
- Stainless steel container and Anode
- 66° C
- 7 Volts
- 1 Minute
- The high pH prevents any plating at all, with the resulting hydrogen gas scrubbing the surface.

4.3 **Rinse: removes and neutralizes NaOH on part.**

- Rinse in Distilled water
- Rinse in "Acid Dip" (**5% Sodium Bifluoride**)
- ~ 1 minute at Room Temperature.
- Rinse in Distilled water

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4.4 Bright Nickel Flash (Woods Strike): To remove any nickel tarnish (NiO or Ni(OH)₂) on surface:

Component	Purpose	g/l	%
35% Hydrochloric Acid	Lower pH	85	8.5%
Nickel Chloride	Source of Nickel ions	225	23%

- Low pH leads to a smooth, thin nickel plating
- 60 C, 3 V, 4 minutes

4.5 Rinse

- Rinse in Distilled water

4.6 Nickel Plating Solutions (“Watt’s” Bright Nickel):

Produces a thick, bright nickel surface.

Component	Purpose	grams/l	%
Nickel Sulfate	Primary source of Ni ⁺² ions	300	30%
Nickel Chloride	Source of chloride ions, which improves conductivity, reducing the voltage needed which helps to prevent water electrolysis and improving efficiency.	66	7%
Boric Acid solution	pH buffering agent	45	4%
10% Sulfuric Acid	Control pH to ~4 Add more as needed	4.2	0.4%
Sodium Saccharin	Small amount – is a brightener	Trivial	~0%

4.7 Nano Powders (<20 nm)

Notice that there are no Noble metals such as platinum or ruthenium used in these recipes.

Nano Powders	Electrode Type	Grams/l	
nFe, nSn, nCo	Cathodic nano powders	3.5, 3.5, 1.8	Grams
nFe, nCo	Anodic nano powders	1.8, 1.0	Grams
nNi, nSn, nCo	Bi-Functional nano powders	3.5, 3.5, 1.8	Grams

- If used for organic digestion or as an alkaline fuel cell, use the “bi-functional” recipe.
- Heat bath with powders to 60° C.
- Measure nano loading using a settling method e.g.: draw into a clear syringe and see the level the solids settle to in 1 minute. Record value. Every two electro-coatings, add nano powders as needed using the ratio in the recipe above.
- Keep particles suspended and flowing THROUGH the porous nickel current collector.
- Monitor pH to keep at ~4 using 10% H₂SO₄ solution, adding dropwise.

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4.8 The Reaction Vessel - Figure 1:

- Pour into a ceramic reaction vessel with a counter-electrode (Anode) both above and below the nickel foam working-electrode (cathode).
- Heat to 60° C and hold it there using a water jacket.
- Circulate to keep nano powders suspended and connect the Anode (+) and Cathode (--) leads
- Run the pulse pattern shown below.
- We used a square ceramic container with the down-tubes in the four corners and one in the center of the sample holder.
- Using the electrolyte flow to keep the particles suspended was Laboratory Assistant Crawford McCarty's notion and it worked perfectly. Originally small agitators were used with poor results due to uneven flow-patterns allowing powders to pile up in small drifts.

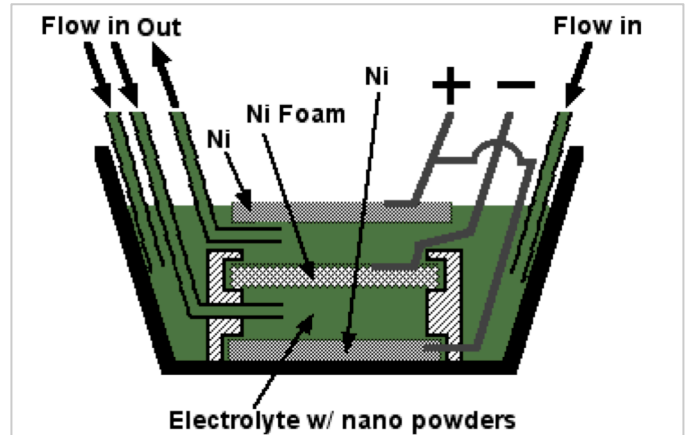


Figure 1. Container is set within a larger square container, situated on a hot-plate acting as a water jacket to maintain the 60° C temperature.

4.9 Plating wave-shape - Figure 2

- Plate using a reverse-pulse plating power supply (e.g.: Dynatronix DPR20-10-30)
 - +30 Amps for 0.5 mSec,
 - 0 Amps for 9.5 mSec (5% duty)
 - -10 Amps for 0.75 mSec,
 - 0 Amps for 0.25 mSec (75% duty)
 - This is 50% ASec stripping
 - Time set to 48.88 minutes (2000 ASec)
 - Remove and copiously rinse in Distilled water.
 - Dry at 100 C in air
 - Reweigh and record.

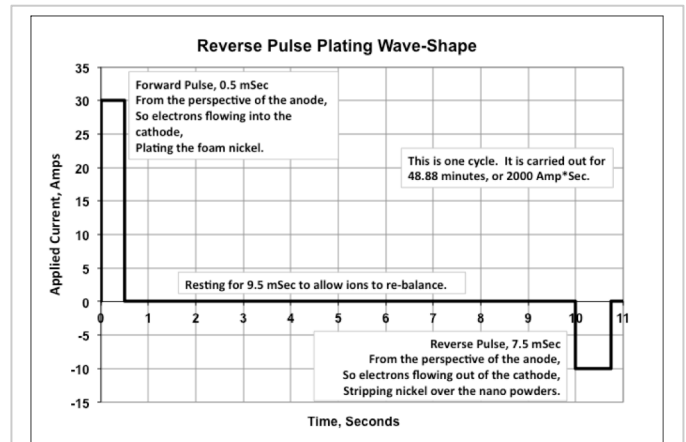


Figure 2

The plating concept is that in the first millisecond or less, nickel ions are evenly distributed throughout the bath and within all pores of the nickel foam, so plating is uniform everywhere, encapsulating the nano powders within that layer. Shortly thereafter, the ions become depleted except on surfaces facing the nickel counter electrode. Thus, the short forward pulse.

Reverse pulses are typically used in plating to produce very smooth surfaces. This is because any raised point on a metallic surface will have a higher current density than the

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flat plane surrounding it and therefore will remove nickel selectively from raised, or rough areas.

In our case, these raised areas hold a nano particle, so the overlying nickel is stripped off the powder. The next pulse repeats this plating and stripping ultimately resulting in the nano powders being fully exposed to the electrolyte but held in tiny nickel bezels, giving extremely low electrical resistance to the nano catalysts. The surface is black do to the exposed nano catalysts.

5. Nano-particle Surface Area Effect

As a material is divided into smaller and smaller particles, the three-dimensional surface area per gram increases logarithmically. For example, a one-gram pellet of nickel is 0.6 cm in diameter and has a surface area of 1.12 cm². One gram of 10 nm particles has a total surface area of 67 m² or 27 feet on a side - a 60 million-fold increase. By mixing particle sizes, the pack-density increases, so even larger surface area gains can be made per volume of particles. This surface area increase improves electrochemical reactions due to the increase in the ratio of surface atoms. Bulk atoms have 12 neighbors and are unattainable to the liquid boundary layer. Surface atoms have 6 to 9 neighbors and are able to interact with their electron clouds in the reactive boundary layer. As **Figure 3** illustrates, this gives nano-coated surfaces more exposure for a higher electrochemical activity.

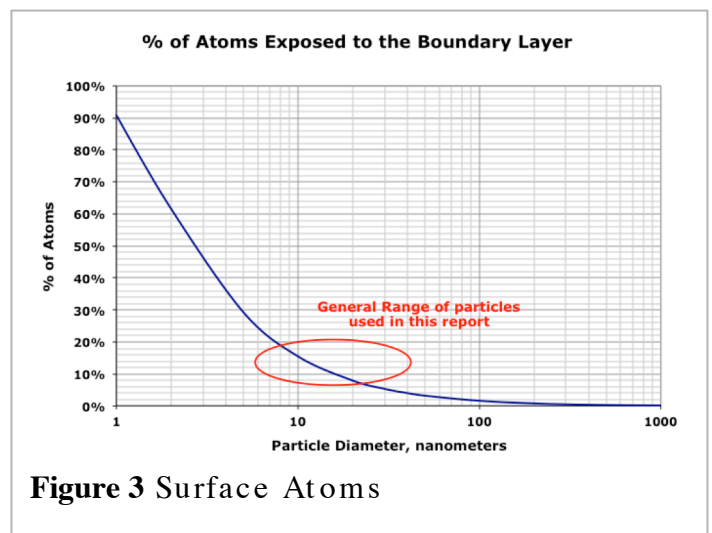
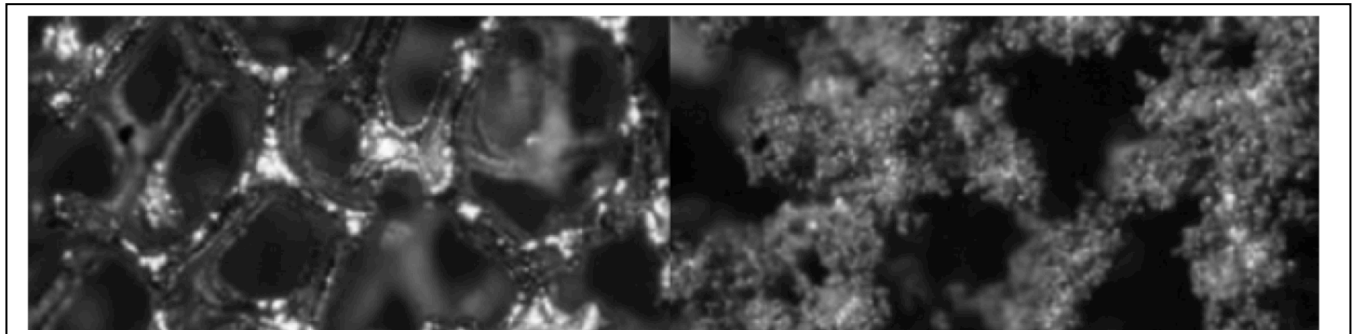


Figure 3 Surface Atoms

6. Resulting coating a Metallic Surface with Nano-catalyst

The techniques to catalyze a nickel current collector for electrolysis is often slow and energy consuming such as Raney Nickel (or similar) applications, sputtering or using thermal flow characteristics of other metals such as silver to act as an adhesive. All of these have serious problems when scaled up for large volume hydrogen production, are energy expensive to make and/or are not robust enough to withstand the rigors of an electrolyzer.

The method outlined above results in the nickel foam surface being fully coated on all intricate surfaces within the foam, thus providing a solid-state 3D reaction surface much like a fluidized bed reactor that is frozen in space. **Fig 4** shows this resulting surface next to uncoated foam.



7. Resulting Performance from Whitepaper <http://bit.ly/1ILRpPE>

7.2 Full Cell Evaluations

The half-cell above was essential for developing the recipes for the anode and cathode because it is specific to the catalyst being studied with no effect of the electrolyte and separator. These data in section 7.2 and 7.3 are from whole cells, so all internal losses are expressing themselves. Over 12 separators were evaluated allowing us the lowest impedance loss from this essential component. **Figure 9** is the full cell voltage of key designs, all using a 3D monopolar design. The lower the voltage, the higher the energy efficiency. A lower voltage also allows for more cells to fit between the voltage rails of the system. For example, 40 cells at 2.117 (70% EE) volt cells will fit in an 85 VDC (rectified 120 VAC) range, while 48 cells at 1.75V (85% EE) will fit within the same constraints. That is a 20% increase in hydrogen generation for each amp that passes through the electrolyzer series stack.

Figure 10 is the same data as **Figure 9** but expressed as the cell Energy Efficiency rather than cell voltage in the dependent axis. **Figure 10** is instructive for the changes shown. The lowest efficiency is a nickel foam electrode with no coating at room temperature. Next the advantage of heating the cell to reduce iR losses is observed. All the rest are at elevated temperature. Next is a commercial Raney Nickel electrode. The top is our present 3D electrode using three transition metal, non-noble, nano-metal catalysts. We still are seeking the best separator, electrolyte additives and perhaps a power supply wave-shape.

Figure 11 compares the hydrogen output as a function of the cost. The graph shows output in kg/Hr and kLiters/hr for a hypothetical electrolyzer running on 240 VAC (170 VDC) and having 100 cm² electrodes as a function of the kWh/kg of hydrogen. This shows that high rate hydrogen outputs are possible at reasonable energy costs.

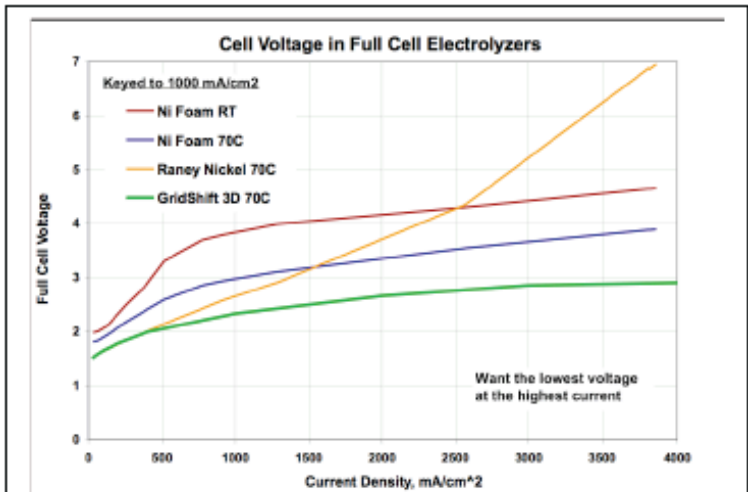


Figure 9: Full Cell Polarization

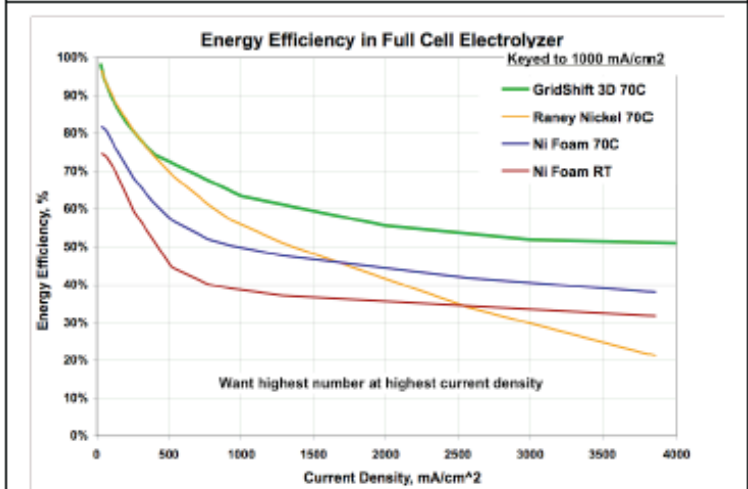


Figure 10: Full Cell Set as %EE

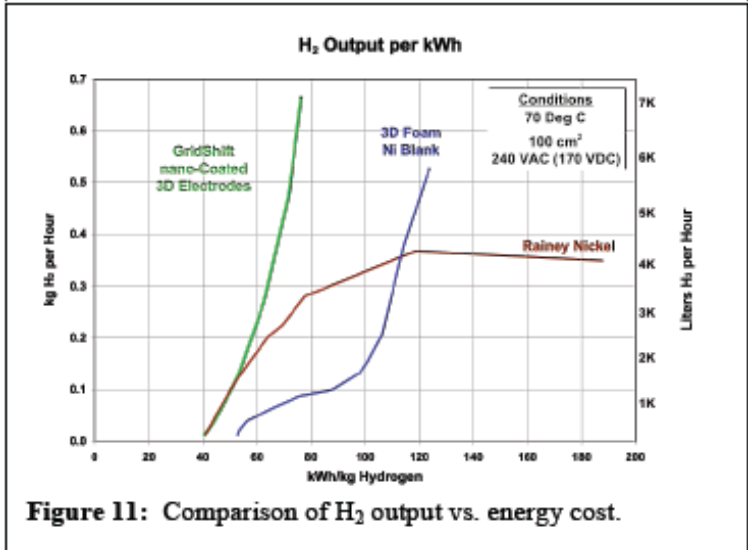


Figure 11: Comparison of H₂ output vs. energy cost.

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7.3 Flat-Plate Bifunctional Cells

There are applications that require flat-plate designs. This is particularly useful in tight spaces like “On Demand” electrolyzers under the hood of motor vehicles. Using this coating process, coated nickel foam panels were welded to SS316 flat-plate bifunctional electrodes. **Figure 12** shows the cell voltage of an electrolyzer using flat SS316 plates (the typical electrodes used today) and with the GSI coated plates. Also shown is the best performing bifunctional electrodes presented at the National Hydrogen Association meeting last year by a large corporation. **Figure 13** shows the same data, but recorded as Energy Efficiency. The advantage of our coating technique is unambiguous.

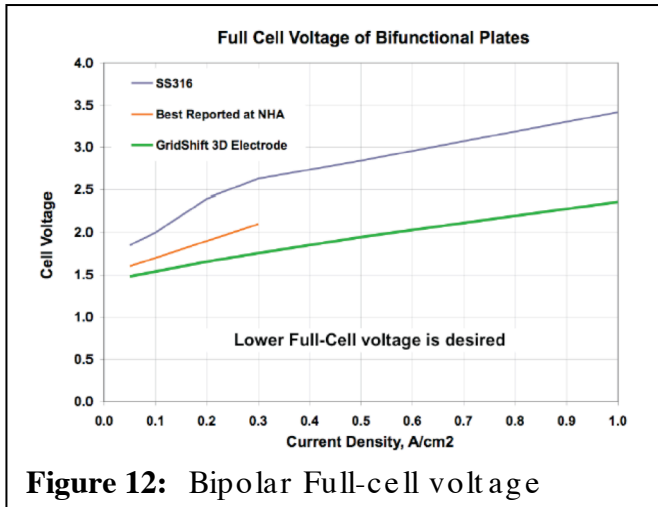


Figure 12: Bipolar Full-cell voltage

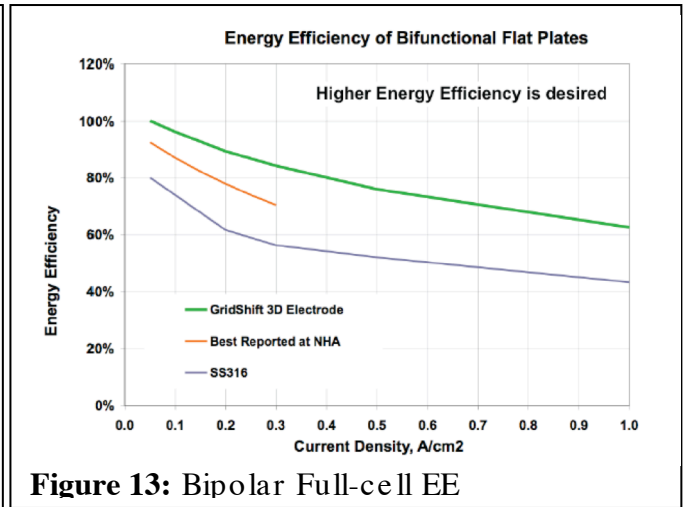


Figure 13: Bipolar Full-cell EE

8. Conclusions

- Our nano-coated 3D electrolyzer is a very high rate, high efficiency water electrolysis unit.
- We have developed recipes for the anode and cathode electrodes using inexpensive, common elements and no precious metals.
- Our coating method covers all surfaces inside and outside of a complex porous electrode greatly increasing the catalytic surface area.
- The electrodes are high rate per geometric surface area, so they can be smaller for the same hydrogen output. This results in stronger electrodes and more compact finished units.
- Our successes are based on full factorial experimental designs and on sound electrochemistry.

9. Acknowledgements

- Senior Laboratory Assistant Crawford McCarty worked tirelessly in the laboratory and contributed greatly to the success of this project. His many insights and imagination proved invaluable to our progress.
- The entity that did this research was the now defunct “GridShift Inc.” which was a subsidiary of DoppStein Enterprises Inc. Funding was a partnership with Khosla Ventures of Palo Alto, CA. We thank Vinod for his support.

10. Profile of Robert Dopp

Robert Dopp, President, DoppStein Enterprises, Inc.

Mr. Dopp is one of the foremost authorities on zinc-air fuel cells and air electrode technologies and a leading expert in the field of water electrolysis and alkaline fuel cells. During his 18-year career as an engineer at Rayovac Corporation, he was a principal developer of the zinc-air hearing aid battery and lead engineer in the development of the air-cathode component.

He then became the Director of Research for Electric Fuel Corporation of Beit Shemesh Israel for five years.

Mr. Dopp has significant expertise in a wide range and depth of knowledge in battery, fuel cell, and hydrogen generation systems. Forming his own R&D consulting firm and laboratory in 2002 (DoppStein Enterprises Inc., DSE), he consults to battery, fuel cell, and hydrogen generation related industries. He has developed components and designs resulting in longer-life batteries with over four times the energy density of alkaline cylindrical cells, and many tens of times higher energy than many rechargeable batteries. His work in water electrolysis is paradigm changing. His onsite laboratory in Marietta, Georgia provides him considerable flexibility, consulting on the electrochemistry and design of gas electrodes and building cathode machines among other development projects. Mr. Dopp has 42 issued patents as of 2016.

As chief scientist and CEO of DSE, Mr. Dopp is working in renewable energy related fields including electrodes for batteries, metal-air fuel cells and hydrogen production through water electrolysis utilizing cutting edge nano-scale catalysts. Mr. Dopp has been a guest lecturer on university campuses and at technical associations including the National Hydrogen Association and Sandia National Laboratories.

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