Electrochemistry and the Future of the Automobile
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ABSTRACT Electrification of the automobile provides a means of sustaining personal mobility in the face of petroleum resource limitations and environmental imperatives. Lithium ion (Li ion) batteries and hydrogen fuel cells provide pure-electrification solutions for different mass and usage segments of automotive application. Battery electric vehicles based on current and targeted Li ion battery technology will be limited to small-vehicle low-mileage-per-day applications; this is due to relatively low specific energy (kWh/kg) and long recharge time constraints. We briefly discuss new generations of Li ion positive and negative electrode intercalation compounds that are needed and under development to achieve energy storage density, durability, and cost targets. Lithium–air batteries give promise of extending the range, but scientists and engineers must surmount a plethora of challenges if growing research investments in this area are to prove effective. Hydrogen fuel cell vehicles have demonstrated the required ~300 mile range and the ability to operate in all climates, but the cost of Pt-based catalysts, a low efficiency of utilization of presently cost-effective renewable sources of primary energy (e.g., electricity from wind), and the development of hydrogen infrastructure present significant challenges. Dramatic decreases in the amount of Pt used are required and are being brought to fruition along several lines of development that are described in some detail.

A realistic aspiration for the special level of freedom provided by mechanized means of personal transportation is spreading to billions more of the Earth's population as developing countries achieve higher levels of economic performance. At the same time, the reserves of easily-recoverable petroleum that have provided remarkably high-energy-density fuels for road transportation systems are being depleted at a growing rate, and the need to constrain carbon dioxide emissions may prevent us from burning those fossil fuels that remain available. Requirements for the protection of the driver and passengers, both against weather and against possible collisions, will place ultimate limits on mass reduction as the primary strategy for reduction of total energy used in automobiles (at least until active collision-avoidance equipment is perfected and universally applied). The efficiency gains obtainable from internal combustion of the type currently in mass production can make modest gains against the problems but cannot of themselves solve the issues of petroleum supply and CO₂ emissions. Electrification of the automobile, when coupled with development of sustainable sources of primary energy, can provide future generations with the continued joy of going where they want, when they want, over distances much larger than those practical for even the most avid bicyclists (who are provided no crash protection). The burning of biofuels in conventional internal combustion engines may provide another option for sustainable transportation; drawing a proper balance between investment in biofuels and investment in abiotic CO₂-neutral energy sources is a complex matter that is outside the scope of this Perspective, which focuses on the potential impact of electrochemical energy systems.

Much of the utilitarian application of automobiles occurs over short distances; 78% of automotive customers commute less than 40 miles daily (total round trip).1 For small vehicles limited only to such day-to-day applications, likely extensions of current-day battery technology may prove adequate without other onboard energy sources. However, much of the joy of a car lies in the owner's ability to just get in and go, go as far as the available time permits with refueling requiring a negligible fraction of the driving time. Moreover, most of the cost of today's vehicle lies in its structure and components other than its powertrain. How many people would be willing to pay full cost for a car that cannot go much farther than that required by an average commute and a few errands before it either needs to be plugged into a normal household circuit overnight or to be hooked to a megawatt power line for 10 min (assuming adequate durability with such rapid charging proves possible)? Battery electric vehicles with these constraints are becoming available for purchase; therefore, we will soon learn the answer to this market-acceptance question.

The soon-to-be-available Chevrolet Volt addresses these issues by carrying a gasoline or biofuel internal combustion-powered generator to allow trips beyond its 40 mile all-electric range. This near-term solution (which with biofuels could essentially eliminate greenhouse gas emissions for trips of all lengths) should allow consumers to become

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familiar with electric vehicles without suffering range anxiety or range and power limitations with an all-battery vehicle at low ambient temperatures. However, this approach suffers from complexity due to the presence of two major power and energy sources, with associated packaging and mass challenges. To fully take the automobile out of the environmental equation, all-electric drives are needed, with the electricity supplied by extended-range batteries or by hydrogen fuel cells, drawing on renewable and/or CO₂-neutral primary energy sources. This Perspective will consider the technical status of and research needs for two classes of vehicular electricity sources, lithium ion batteries and hydrogen fuel cells.

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On-Board Electricity Supply Systems. In a world of liquid-fuel-based propulsion, we think in terms of miles per gallon or liters per 100 km. In a world of electrified propulsion, it is helpful to think in terms of Wh/mile. Figure 1 shows a simple schematic of an electric vehicle energy conversion system in which DC electrical energy is provided on-board and converted to mechanical energy through a DC/AC inverter, motor, and gearbox. Electrical energy can come from a battery, a H₂ fuel cell, an internal combustion engine (ICE) with a generator, or a combination of these elements. In this Perspective, we consider only the first two local-emission-free electron sources. The double-sided arrows represent regenerative braking in which braking energy is recaptured and stored, and this quantity depends strongly on the drive cycle. In the analyses below, we will consider regenerative braking to be done using a battery, although there are other approaches, such as flywheels, that have been considered. The Wh_{net}/mile, the total gross energy consumed minus the energy recovered from regenerative braking, determines how much electrical energy must be available on board and is provided by the energy storage/generation system to travel a given range prior to refueling. The ancillary loads, including heating and cooling for passenger comfort, are powered from the electricity storage and generation system and can become major drains of energy that can significantly affect the driving range.

The Wh_{net}/mile requirement to the electric motor depends primarily on the vehicle mass (m) as driven (including the mass of the powertrain system and passengers), the frontal area (A), the drag coefficient (C_d), and the drive cycle. The requirement also depends heavily on the rolling resistance and ancillary loads, which we have assumed to be constant and representative of future high-efficiency vehicle technology. This relationship can be correlated for a wide range of vehicle parameters using the simple equation shown below

\[ \text{Energy required} = a_1 \times m + a_2 \times C_d \times A + a_3 \]  

in which \(a_1\), \(a_2\), and \(a_3\) can be obtained through regression of modeling results from a fully dynamic vehicle system model based primarily on the GREET (the greenhouse gases, regulated emissions, and energy use in transportation) software developed by the Argonne National Lab, and these constants depend on the drive cycle. In Table 1, we list estimates beginning with a small subcompact car (\(C_d \times A = 0.6 \text{ m}^2\)) with a total vehicle mass of 1200 kg for which the energy required to drive the EPA (Environmental Protection Agency) city or highway cycle is 138 or 156 Wh_{net}/mile, respectively. For a van-like people mover vehicle (\(C_d \times A = 1.56 \text{ m}^2\)) with a mass of 2500 kg, the energy required is 283 or 361 Wh_{net}/mile for the city or the highway cycle, respectively. Note that the energy requirement for an electric vehicle is actually less for city as compared with that for highway driving, the opposite of our experience with conventional ICE vehicles. This is because the electricity generation source is more efficient at lower loads, the vehicle has less resistance to overcome at lower speeds, and the use of regenerative braking preserves these advantages for the city cycle. The vehicle type-to-mass relationships in Table 1 are consistent with typical values for current ICE-powered vehicles.
We now estimate the specific energy for each of these systems using the assumptions in Table 2. Each system has sufficient power to provide acceptable 0–60 mph performance (<10 s) for a compact vehicle such as the Chevrolet Volt design. On technology stretch assumptions, we assume that USABC (United States Advanced Battery Consortium) and DOE (U.S. Department of Energy) development targets are achieved as shown in the table, values we believe to be reasonable estimates of the potential of each technology.

In Figure 3, we plot estimates of the specific energy of these systems versus the net energy required. For the battery pack, additional energy is provided by adding cells of the same design; the usable specific energy is consequently independent of energy required. The value of 152 Wh/kg is based on the 200 Wh/kg USABC target, assumes that 80% of the state-of-charge (SOC) window is available for use in order to meet minimum power at a high depth of discharge requirements, and reflects a 95% efficiency discharge. In addition, we show the estimated specific energy of the battery packs used in soon-to-be-released commercial battery electric vehicles assuming ~120 Wh/kg (24 kWh and 200 kg for Nissan Leaf, 2 53 kWh and 450 kg for Tesla Roadster3), a 80% SOC window, and 95% discharge efficiency. In contrast to the pure battery systems, the specific energy of the fuel cell system increases with energy required; in these systems, energy is added through additional H2 on the vehicle with a larger tank. At energy requirements below about 32 kWh (sufficient for a 170 miles range for the compact vehicle referenced in Table 1), the battery offers a higher specific energy. Above 32 kWh, the FCEV system is preferred from this system-mass standpoint.

With this background, we now estimate for various options the mass required to provide electricity to achieve 100 and 300 mile ranges for vehicles of a variety of sizes, and the results are shown in Figure 4. The mass shown on the x-axis is the base vehicle mass of the electric vehicle not including the mass of the energy storage/conversion system shown in Figure 1 but including the mass of the inverter, the drive unit, and the passengers. The total mass of the vehicle as driven will be the sum of the base vehicle mass shown on the x-axis and the incremental mass shown on the y-axis. This total mass is used to determine the test weight class for fuel economy tests. The energy requirements used in this analysis are based upon the empirical correlation shown earlier, using the EPA city drive cycle and solved iteratively to account for the mass of the electricity storage and generation system. Additionally, the system power was scaled with vehicle mass to give acceptable acceleration (8–10 s for 0–60 mph) for all vehicle types. As the mass of the energy storage/conversion system increases, this forces additional mass on to the vehicle as well to support the system. This additional structural mass, assumed to be 40% of the energy storage/conversion mass, was added to the mass of the electricity-generating system to give the incremental mass plotted on the y-axis in Figure 4. For the 100 mile range option, battery power is lighter for all vehicle sizes. With increasing vehicle mass, the mass of the fuel cell system increases because of the added power required to meet the acceleration requirement, thereby maintaining the gap between the 100 mile BEV and the FCEV shown in Figure 4a. At the 300 miles range, the battery-powered option becomes heaviest even for small vehicles, and the fuel cell option is then the preferred approach for full electrification. In summary, it is this fundamental dependence of the specific energy on the amount of electricity required, shown in Figure 3, which determines the

Table 1. Electrical Energy Required As a Function of the Vehicle Type and Mass

<table>
<thead>
<tr>
<th>Vehicle Type</th>
<th>Mass (kg)</th>
<th>Cd × A (m²)</th>
<th>City (Wh-net/mile)</th>
<th>Highway (Wh-net/mile)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sub-compact</td>
<td>1200(2)</td>
<td>0.60</td>
<td>138</td>
<td>156</td>
</tr>
<tr>
<td>Compact Car</td>
<td>1400(4)</td>
<td>0.64</td>
<td>154</td>
<td>171</td>
</tr>
<tr>
<td>Mid-size Car</td>
<td>1550(4)</td>
<td>0.67</td>
<td>166</td>
<td>183</td>
</tr>
<tr>
<td>Full-size Car</td>
<td>1700(5)</td>
<td>0.71</td>
<td>178</td>
<td>194</td>
</tr>
<tr>
<td>Minivan</td>
<td>2200(7)</td>
<td>0.93</td>
<td>224</td>
<td>250</td>
</tr>
<tr>
<td>Van</td>
<td>2500(8)</td>
<td>1.56</td>
<td>283</td>
<td>361</td>
</tr>
</tbody>
</table>

Note: Analysis assumes 70% recovery of braking energy through regenerative braking. The mass includes the number of 65 kg passengers shown in parentheses.
The applicability of these systems in vehicles of various size and range. This allows batteries for small low-range pure electric vehicles but excludes them for larger-vehicle long-range applications. Previous studies comparing BEVs and FCEVs\textsuperscript{7,8} have reached similar conclusions that only limited-range BEVs are workable, with somewhat different crossover ranges between BEVs and FCEVs arising from different input assumptions for the two technologies.

**Figure 3.** Electricity generation specific energy as a function of total energy required based on an 80 kW system with the specifications listed in Table 2.

**Table 2.** Storage and Electricity Generation Systems and Assumptions

<table>
<thead>
<tr>
<th>configuration</th>
<th>main electricity generator</th>
<th>energy storage</th>
<th>hybrid battery</th>
</tr>
</thead>
<tbody>
<tr>
<td>battery electric vehicle (BEV)</td>
<td>80 kW, 40 kWh, battery, 95% efficient discharge\textsuperscript{a}</td>
<td>battery, 80% of rated charge utilized\textsuperscript{a}</td>
<td>not needed</td>
</tr>
<tr>
<td>fuel cell electric vehicle (FCEV)</td>
<td>80 kW fuel cell system, 57% efficient\textsuperscript{a}</td>
<td>700 bar H\textsubscript{2} storage\textsuperscript{c}</td>
<td>40 kW, 1.7 kWh, 50% of rated charge utilized\textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Meets USABC long-term goals for advanced batteries for EVs (300 Wh/L, 200 Wh/kg).
\textsuperscript{b} Meets DOE 2015 goals for fuel cell systems (650 W/L, 650 W/kg).
\textsuperscript{c} Meets DOE 2015 H\textsubscript{2} storage system goals of 1500 Wh/L and 1800 Wh/kg based on a lower heating value of hydrogen of 33.3 kWh/kg, translating to 4.5\% hydrogen stored on a mass basis.
\textsuperscript{d} Meets USABC 2015 goals for a maximum power-assist battery (45 L, 60 kg).

**Figure 4.** Projected incremental mass due to the energy storage and electricity generation system for (a) the 100 and (b) 300 mile range for a battery electric vehicle and a fuel cell electric vehicle.
implemented in full-scale batteries, full-range recharge in a
time equivalent to pumping gas into a internal combustion
vehicle requires tapping power in the 1–20 megawatt range
from the grid for each vehicle being charged, thus potentially
constraining the location of rapid recharge stations. Because
the charging efficiency decreases at high rates, rapid recharge
stations would also have to provide active liquid cooling for the
battery during charge. Li ion batteries provide a pathway for
efficient use of renewable-sourced electricity in the transpor-
tation sector, but it is possible that fundamental physical
limitations may prevent pure Li-ion-based BEVs from ever
delivering the freedom of providing long trips, with inter-
mittent quick refills, that consumers currently receive from
their cars.

In addition to mass considerations, alternative powertrain
feasibility is determined by packaging (i.e., volume) consid-
erations. Once physical feasibility is established, commercial-
ization is ultimately determined by cost. Packaging and high-
volume cost analyses of projected technologies are outside of
the scope of this Perspective. Solely on the basis of the mass
considerations above, we can conclude that battery-powered
options are favored for small vehicles when short-range and
long refueling times are acceptable. The fuel cell option is
favored for large-vehicle, long-range options.

Lithium-Based Secondary Batteries. Lithium ion batteries
have the advantage of ~90 % charge/discharge roundtrip
energy efficiency (up to approximately 1 h charge rates),
allowing them to make efficient use of electricity generated by
relatively expensive renewable primary energy sources such as
wind and solar. Current Li ion battery technologies for
batteries electric vehicles, as described above, have a specific
energy of ~120 Wh total/kg pack, needing further improvement
to reach the short- (150 Wh total/kg pack) and long-term (200
Wh total/kg pack) advanced battery goals established by USABC.

What is it that is determining the specific energy of today’s
Li ion batteries? Figure 5 shows an estimate of the kg/kWh total
of various pack elements, with key material assumptions for
the estimates shown in the inset table. USABC short- and long-
term total pack targets are also shown. (Note that plotting the
inverse of the common specific energy metric allows visuali-
ization of the mass contributors to the pack.) Using numbers
given in the inset for the cell materials, we estimate that about
50% of the mass is due to the cell materials, and ~70% of the
cell material mass comes from the positive and negative
electrode materials. Thus, the primary mass reduction focus
needs to be on improving the specific energy of the positive
and negative active materials, in priority order. The pack
components indicated in Figure 5 include components to
provide mechanical support, thermal control, and electrical
control. We estimate these by the difference to comprise
approximately 50% of the pack mass. Although reductions in
pack component mass will be an important element of
reaching USABC targets, within the scope of this Perspective,
we will focus on the need for energy storage materials that
have higher gravimetric energy densities in order to drive cell
mass reduction.
Figure 5 suggests that the mass of today’s technology must be decreased to 80 and 60% of today’s values to meet the short- and long-term targets, respectively. However, these targets also require use of 80% of the SOC window over the lifetime, and it is not clear if this will be achieved in initial commercial offerings. To the extent that less than 80% of the SOC window is used in order to ensure durability, this represents an additional technology gap that must be closed either through material durability or further charge-storage improvements.

The largest contributor to the battery mass is the positive electrode material, as shown in Figure 5. State-of-the-art materials include LiMn2O4 electrode material, as shown in Figure 5. State-of-the-art improvements. Either through material durability or further charge-storage represents an additional technology gap that must be closed.

The largest contributor to the battery mass is the positive electrode material, as shown in Figure 5. State-of-the-art materials include LiMn2O4, LiNi0.5Mn1.5O4 (180 mA–g active), and LiFePO4 (160 mA–g active) and variants, as summarized in monographs and reviews. To achieve mass reduction, new materials are needed with higher storage capacity and/or with substantially higher voltage, the latter being a direction that would also require development and implementation of electrolytes/solvents with improved oxidation resistance. One example of a promising direction is through the development of materials that enable the intercalation of more than one Li ion per transition metal, as contrasted with one Li ion per transition metal possible with the state-of-the-art materials listed above. For example, the insertion of two Li ions per transition metal is, in principle, possible with Li metal silicates such as the Mn silicate shown below, with a 333 mA–g theoretical capacity.

$$2\text{Mn}^{IV}\text{SiO}_4 + 4\text{Li}^+ + 4e^- \xrightarrow{\text{Discharge}} \text{2Li}_2\text{Mn}^{II}\text{SiO}_4$$

These materials are the subject of development work, but efforts to date have not yet yielded high-capacity durable materials that are ready for serious implementation efforts. The efforts of inorganic synthetic chemists and solid-state materials experts are needed to address these critical development challenges.

The negative electrode also provides opportunity for mass reduction. The current negative electrode is graphite, with a mass charge capacity of 372 mA–g active (LiC6). Many materials offer theoretical capacities that are higher than that of graphite but with the trade-off that swelling upon Li uptake is higher as well, leading to durability challenges. As an example, substitution of silicon for carbon as the storage material could theoretically increase the negative active material mass charge capacity to 3750 mA–g active (Li4Si).

$$\text{Li}_4\text{Si} \xrightarrow{\text{Discharge}} \text{Si} + 4\text{Li}^+ + 4e^- \xrightarrow{\text{Charge}}$$

However, alternate forms or additional conductive diluents required in the Si-based negative electrode (in large part to deal with the ~4× volume expansion upon charge) mean that the actual charge capacity gain for the complete negative electrode would likely be 30–70% of this. Whereas the high capacity of alternatives to carbon is a well-proven concept, how to do this while not fracturing materials over the cycle life, thus leading to poor durability, is not. To solve this multi-disciplinary problem, the skills of materials design and solid-state synthetic chemists are needed, together with the talents of those expert in the mechanics of materials.

Using cell models of new positive and negative electrode material concepts such as those described above, we estimate that the USABC target of 200 Wh_total/kg_pack is challenging but achievable. This will also require that the mass of the pack components be reduced by a factor of approximately 2 relative to state-of-the-art, an engineering and materials challenge that we consider achievable but outside of the scope of this paper.

We now revisit Figure 4 to estimate the incremental mass for a compact BEV able to drive 300 miles (EPA city cycle) before recharging, assuming that the USABC long-term battery target is achieved. We estimate that for a compact vehicle shown in Table 1, the sum of the mass of the ICE and gas tank required to power it is approximately 150 kg heavier than the sum of the mass of the required inverter and drive motor. Thus, the base vehicle mass (Figure 4 x-axis) of a compact electric vehicle will also be 1250 kg (including four passengers), and Figure 4b shows an incremental mass of 220 or 480 kg for the fuel cell or battery-powered options, respectively. The latter option consists of 340 kg for the battery pack and 140 kg of added vehicle mass to support the battery. This battery has 68 kWh_total and 52 kWh_usable (80% SOC window, 95% discharge efficiency). This translates to 173 Wh_net/mile (compared to 154 Wh_net/mile shown for a compact vehicle in Table 1); the significant incremental battery mass pushes the vehicle energy requirement from the compact into the mid-size vehicle range, as shown in Table 1.

To recharge the 300 mile compact BEV in the less-than-5 min “refueling” to which we have grown accustomed, a charger power of > 0.6 MW is required. A 5 min refill corresponds to a 12C rate, which is likely to drive charge efficiencies to less than 85%, resulting in battery internal heat generation in the 100 kW range. This will drive cost into the thermal system and challenge materials durability. Because of the mass and refuel time issues, we see the best fit for Li-ion batteries, much smaller versions of them, as an element of a powertrain employing an internal combustion range extender.

We now turn our attention to energy storage/conversion chemistries beyond Li ion “rocking chair” batteries comprising Li storage compounds on both the positive and negative electrodes. The most well-known concepts include Li–sulfur and metal–air batteries. The Li–sulfur system, which relies on the use of low-cost sulfur on the positive electrode, has promising specific energy because of the potential for storage of 2 moles of lithium for every mole of sulfur. The major challenge is that the sulfur is soluble in the electrolyte when not fully oxidized and is subject to migration and reduction on the negative electrode. Metal–air systems (e.g., Zn–air, Li–air) are also in the spotlight once again because of the appeal of using air instead of a problematic and expensive positive electrode intercalation material. We now consider these in the next section, with special focus on Li–air, which has been gaining a tremendous amount of recent attention and funding.
Lithium–Air Batteries: Airliners are powered by jets, not rockets, for good reasons. The oxidizer (liquid oxygen) comprises 83% of the mass of the space shuttle’s external tank before liftoff, compared to only 14% for the fuel (liquid hydrogen). Unlike most of the universe, the earth’s surface is rich in oxygen. Its inhabitants would be foolish not to take advantage of this resource for terrestrial transportation. Classical batteries carrying both “fuel” (reduced material) and “oxidizer” (oxidized material), contributing to their chronically low energy densities, are analogous to the rocket. Primary metal–air batteries, the electrochemical analogue of the jet engine, find current application in such low-power devices as hearing aids, replacing environmentally unacceptable mercury cells. In the form of “mechanically recharged” (i.e., primary) zinc–air or aluminum–air batteries, they have periodically been studied for possible automotive powertrain applications and have been rejected for causes including low energy efficiency of metal production, excessive self-discharge, and the logistical difficulty of returning the product slurry of metal hydroxide to central processing plants to regenerate the metal fuel.

A large research effort is currently spooling up to try to develop true secondary Li–air batteries. In the positive electrode of a standard Li ion battery, Li ions intercalate into an oxygen-containing compound (e.g., oxide, phosphate) of another metal (e.g., Co, Mn) during discharge, reducing the effective oxidation state of that other metal. This standard chemistry gives positive electrode (e.g., LiMn2O4, 0.85 g_{electrode}/molar) mass energy densities of ~490 mWh/g_{electrode}, and this factor significantly impacts the mass-specific energy of the entire battery, as shown in Figure 5. In the discharge of the positive electrode of a lithium–air cell, the lithium transported from the negative electrode reacts (typically on a carbon support with or without additional catalysts) with atmospheric oxygen to form a lithium oxide. The composition of this oxide remains a matter of debate, mostly lithium peroxide (Li2O2) by ex situ Raman spectroscopy but with some Li2O indicated by oxygen consumption studies. The projected specific energy of Li–air positive electrodes, when normalized to the mass of the air–electrode carbon support, can be estimated (assuming a 2.75 V cell voltage) as a quite impressive 12700 mWh/g_{electrode} assuming Li2O2 or 16500 mWh/gC assuming Li2O, about 25–35 times conventional Li ion positive electrodes. However, for Li–air, the incorporated oxygen constitutes a large fraction of the total discharged positive electrode mass, so that the advantage per mass of total electrode is much less for a discharged system. The projected advantage in mWh/g_{electrode} for Li–air (assuming a Li2O2 discharged state, 2450 mWh/g_{electrode}; Li2O, 3700 mWh/g_{electrode}) is 5 (Li2O2) or 8 (Li2O) times that of more conventional non-air-breathing positive electrodes. Since vehicle batteries will typically be in a varying intermediate state of charge, care must be taken in estimating the projected range benefits of Li–air batteries, though on this simple theoretical positive material mass basis, they remain substantial. Going from this material-based analysis to a practical system requires the addition of flowfields and manifolds required to get the O2 in and out of the system as well the balance of plant (compressor and gas conditioning needed to support it). These must be considered when evaluating the net result of a Li–air system at the vehicle level.

The above consideration relates to energy storage capacity, but substantial improvements in rate capability are required for Li–air systems to become practical. The Li–air positive electrode has some similarities to the hydrogen fuel cell positive electrode in that air must be serviced to each via flowfields. For fuel cells, a geometric power capability of 1 W/cm2 has been successfully demonstrated, requiring ~10 m2 for full automotive power (100 kW) application. For Li ion cells, the geometric power capability is in the 30 mW/cm2 range, requiring 30 times the surface area (about 300 m2) for a 100 kW power (BEV or EREV) application. For state-of-the-art Li–O2 (not air), demonstrated current and power densities for which theoretical capacity is achieved are ~0.1 mA/cm2 and 0.3 mW/cm2. This would require more than 30000 m2 of cell area that would need to be serviced, even with pure O2, for 100 kW power, and such a unit would not fit in a vehicle. Higher current (~1 mA/cm2) and thus power (~3 mW/cm2) densities have recently been reported, albeit with significantly reduced capacities; this would still require packaging of more than 3000 m2 of active area. In order to keep the cell active area requirement in the neighborhood of what is achieved with today’s Li ion cells, important from a system volume point of view, charge and discharge rates have to be improved still further to approximately 10 mA/cm2, 2 orders of magnitude higher than high-capacity performance to date, and this would need to be achieved with air and not O2. Thus, unless a much higher rate capability can be achieved while retaining efficiency, Li–air will not be feasible for vehicle applications.

Even if the electrochemistry can be made to work reversibly and durably, there are many other significant practical issues with Li–air implementation; each of these will add mass, volume, and cost to the overall system. For an open system, provision must be made to ensure that water vapor, nitrogen, oxygen, and carbon dioxide do not contact the negative electrodes of a Li–air battery (or CO2 or H2O for the positive electrodes), leading to some schemes involving thin glass layers giving further limitations on Li ion conductivity and others involving air-scrubbing systems. The open system will require a compressor, gas intercooler, and thermal system at the cost of substantial mass and ancillary load over what is required for the Li ion. There must be a means to ensure acceptably low losses of electrolyte through evaporation over vehicle life as well as means to ensure heat management and safe handling of O2 during the charge steps.

In summary, Li–air cells pose fascinating scientific questions of the thermodynamics and the catalyzed kinetics of interactions of lithium with oxygen. For example, different catalysts may be needed for discharging and charging, and these catalysts must be able to coexist in the positive electrode without poisoning one another. Given the low levels of reversibility and low capacities at high current density demonstrated to date, Li–air cells will likely show impressive percentages of improvement in a number of metrics in the coming years. It is critical that enough attention also be given to fundamental engineering issues and to the absolute, not relative, metrics that reflect product requirements of a
full-function BEV. We are supportive of work on developing reversible Li–air and other advanced electrochemical energy storage systems while keeping the scientific development connected to vehicle developers who understand implementation realities.

It is important to keep the scientific development connected to vehicle developers who understand the implementation realities.

Hydrogen Fuel Cells. Fully functional automobiles powered by hydrogen fuel cells have been built by several manufacturers, with over 1350,000 miles having been accumulated by the General Motors fleet of 116 vehicles, assigned to over 100 customer drivers to use in their daily lives for periods of ~2 months (Figure 6). Operating ranges greater than 300 miles have been demonstrated using hydrogen stored at 700 bar, a technically feasible approach that would benefit from significant reduction in the cost of high-tensile carbon fiber. Fuel cell vehicles can start reliably from subfreezing temperatures, with a brief, self-heating operation possible at low temperatures which bridges to the continuous operation that becomes possible as soon as the stack warms past 0 °C. The stack can then bootstrap itself (and the passenger cabin) to full operating temperatures using the unfortunate, but at times useful, waste heat generated by the kinetically slow oxygen reduction reaction (ORR). The 700 bar hydrogen tanks can be refilled in 3–5 min if the H₂ is precooled to −40 °C. Proper combinations of materials choices and operating protocols are bringing durability close to the expectations of the driving public, with pathways to closing the remaining gaps being visible.

While fuel cell vehicles promise the functionality of current automobiles in an environmentally sustainable form, the issues of (1) hydrogen supply and (2) fuel cell system cost remain significant. Hydrogen is an energy carrier that can be produced from either nonsustainable or sustainable primary sources of energy. At present, hydrogen is made primarily from natural gas. Complete-cycle analysis suggests that the natural gas → hydrogen → fuel cell vehicle process compared to the petroleum → gasoline → internal combustion vehicle process would give (per mile traveled) a 41% reduction in total primary energy use, a 56% reduction in greenhouse gases, and a 100% reduction in petroleum use. In the United States, complete conversion of transportation petroleum use to natural gas via H₂ fuel cells would require a ~60% increase of natural gas production and would be expected to decrease from 70 years to 45 years, the time required to consume the Energy Information Administration’s 1747.47 standard cubic feet estimate of “total technically recoverable natural gas”. Hydrogen from coal, with CO₂ sequestration, is a longer-duration solution that hinges upon the feasibility of long-term disposal of CO₂. Purely thermal processes for generation of hydrogen from nuclear or solar concentration heat are possible but remain in an early stage of development. Direct production of hydrogen by biological organisms is being investigated. Living things seem to show a reluctance to do this efficiently, but some species of algae, when deprived of sulfur, generate hydrogen at least temporarily.

When one thinks of sustainable hydrogen, one tends to think of the combination of sustainable electricity and electrolysis, and herein lies a shortfall of fuel cell versus battery approaches. The electricity to 700 bar H₂ efficiency of (room-temperature) electrolysis is only 63%, and in addition, the fuel cell system is only 50–60% efficient H₂ to electricity.

Figure 6. Customers refueled their GM fuel cell vehicles with hydrogen throughout the winter. Photo by General Motors Field Service Group.
This ~35% net efficiency is in contrast to Li ion batteries that can achieve 80–90% electricity in/electricity out. High-temperature electrolysis (which would perhaps best be matched with nuclear primary energy) could bring the hydrogen fuel cell closer, but a greater than factor of two gap will remain. Some fuel cell proponents have argued that the low efficiency of electrolysis does not matter if the electricity is from a renewable source, but such an attitude ignores the very real and quite high capital costs of renewable electricity. One fact that may close the gap of the steady-state analysis is the fact that renewable sources are intermittent, and making H2 for transportation could be an effective way to deal with this intermittency without having to accommodate it on the grid. For fuel cells to further close this gap, improvements in hydrogen generation from sustainable sources, for example, in the catalysis of the oxygen evolution reaction and/or demonstration of CO2 sequestration to enable the use of coal, would have impact.

Much of the current high cost of demonstration fuel cells arises from manufacturing issues amenable to major reduction through economies of scale. However, baseline costs of some materials in fuel cells, particularly platinum, currently total to an amount equal to a large fraction of the total cost of current internal combustion engines, and Pt cost would tend to increase at higher usage volumes. The platinum content therefore constitutes a lower limit to the cost of mass-produced fuel cells. The kinetics of hydrogen oxidation are so rapid7-9 that anode Pt loadings can be as low as 0.01 mgPt/cm² without measurable kinetic losses on the anode. While electrode poisoning can be an issue at such low loadings, during automotive operation the potential of the anode will vary from that of the reversible hydrogen electrode (RHE) during operation to (during extended shutdown) the > 1.0 V RHE open-circuit potential obtained when both anode and cathode manifolds become filled with air. Such potential swings periodically clean the electrodes of even such otherwise pernicious poisons as sulfur, thereby enabling anode Pt loadings low enough to have no real economic impact. The cathode is another matter entirely. The kinetics of the oxygen reduction reaction (ORR) are notoriously slow (and therefore have received the attention of generations of generally frustrated, though recently more gratified, electrochemists), leading to the current necessity of using ∼0.4 mgPtnm² of geometric loadings of commercially optimized Pt/carbon black cathode catalysts, costing several thousands of dollars per vehicle. Previous reviews34 have set a target of a 4-fold improvement in oxygen reduction activity versus the 0.1 A/mgPt, and 200 µA/cm²Ptnm² at 900 mV (80 °C, H2/O2, PO2 = 100 kPa abs, 100% RH) seen for state-of-the-art Pt/C catalysts. The future prices of platinum group metals (PGMs) cannot be accurately predicted; therefore, to ensure that the fuel cell garnersthe nontrivial place in the automotive market, it seems advisable to target total PGM costs no higher than those needed for catalytic converters for advanced internal combustion engines meeting ever-tightenergycity and emissions standards. This criterion requires about an 8-fold mass activity improvement from that seen for state-of-the-art Pt/C. Since current fuel cell catalysts already constitute a highly developed nanotechnology that packs in an impressive 3.2 x 10²⁰ active sites per cm³ of electrode34 (a major factor that made possible fuel cells small enough to fit in cars), the task seems daunting, but several pathways to the requisite activity appear available. Gasteiger and Markovic have published a brief review that discusses the experimental status of most of the concepts described below, but only from the perspective of turnover frequency (activity per active site).35 On the theoretical side, density functional theory calculations have pointed out a guideline for improving ORR kinetics; one sees surfaces binding oxygen-containing adsorbates a bit more weakly than do Pt nanoparticles.36 One variant of this is the idea that ORR activity increases with a decreased coverage of OH_ads blocking species.37 These rationales for the development of more active ORR catalysts are widely, but not universally, believed. The group of Masahiro Watanabe has concluded from XPS analysis of electrodes emersed from electrochemical cells and transferred into ultrahigh vacuum that higher ORR activities correlate with increased coverages of an O_ads-like species more prevalent at a given potential when the electrolyte is charged with molecular oxygen.37

Continuous-Layer Catalysts: The current Pt/carbon black catalysts, as illustrated in Figure 7a, were developed by constantly pushing toward higher catalyst dispersions at higher wt % Pt, but the physical limits of this approach may have been reached. One pathway to higher Pt mass activities that has demonstrated some success involves moving in a direction diametrically opposed to this quest for high dispersion. Unlike many surface reactions that occur more rapidly on low-coordinated surface sites such as steps and kinks, the oxygen reduction reaction gives a 5- to 10 fold higher area-specific activity (per surface Pt atom) on the smooth surface of a ~6 nm diameter Pt disk than that on the vertex- and edge-atom-rich ~3 nm diameter Pt nanoparticles of commercial Pt/C catalysts.34 Similarly, in the Pt nanoparticle range, higher area-specific ORR activities are often seen on larger rather than on smaller particles,38 though some controversy remains about the “particle size effect” over 1–5 nm.39 The high specific activity of continuous Pt surfaces has found practical application in 3M’s nanostructured thin film (NSTF) catalysts40 (Figure 7b), in which a thin (~8 nm on average) continuous Pt or Pt alloy layer is deposited over a moderate surface area support (~8 cm²/cm² of geometric) consisting of nonconducting organic whiskers. In its current manifestations, NSTF delivers 5–10-fold-enhanced Pt-area-specific activities (vs Pt/C) similar to those of flat Pt disks, compensating for a smaller percentage of total Pt atoms on the surface versus small nanoparticles. It thereby achieves Pt mass activities roughly equivalent to those of standard dispersed Pt/C catalysts. Several pathways to higher mass activities would appear to be available with the NSTF approach, including growing continuous layers at smaller mean Pt thicknesses. Unfortunately, due to the high surface free energy of Pt, this is easier said than done, and the deposition of thin, continuous metal layers is a challenging research area in its own right.41 Continuous-layer catalysts can be expected to be more resistant than nanoparticle catalysts to loss of activity due to Pt dissolution and redeposition during the voltage cycling accompanying automotive duty cycles, an expectation that has
largely been borne out with NSTF, though the approach faces other durability challenges including a higher sensitivity to contaminants. In its current configuration, the NSTF electrode is about 30 times thinner than the 10 μm typical of Pt/C cathodes. Such thin electrodes are susceptible to flooding by liquid water produced in the fuel cell, leading to operational challenges in low-temperature and transient operation that are subjects of continuing engineering development. Other continuous-layer catalyst systems are under study but are not yet at as advanced of a stage as is NSTF.42

Pt Alloy and Dealloyed Catalysts: Pt alloy catalysts have been used for decades in phosphoric acid fuel cells, primarily from considerations of durability at elevated temperatures. In polymer electrolyte fuel cells, Pt alloyed with metals such as Cr, Fe, Co, Ni, Ti, and W at a stoichiometry around Pt3M has typically given Pt mass activities around 0.2 A/mgPt, ~2 times higher than those of pure Pt/C,34 with occasional outliers of higher activity. Recently, initial ORR activities consistently > 4 times that of Pt/C have been reported by the group of Peter Strasser for PtCu3 particles, from which most of the copper has been removed by repeated electrochemical potential cycling in aqueous acid.43 The original explanation for this effect, based on X-ray diffraction measurements of lattice parameters and EDAX estimates of copper content (the latter likely compromised of a high background from microscope components), was that removal of essentially all of the copper, at least from the top ~8 atomic layers, left a pure Pt surface with a lattice parameter that had not completely relaxed from the smaller lattice spacing in the original Cu-rich alloy. Density functional theory calculations suggest that such lattice compression should lead to changes in the electronic structure of the surface Pt atoms,44 which should be beneficial to ORR activity. However, more recent work at GM and elsewhere has shown that similarly enhanced initial activities can be obtained with particles retaining higher copper content, for which advanced scanning transmission electron microscopies (STEM and analytical microscopy) show two types of particles present, (1) Pt shells about 3–5 monolayers thick surrounding a copper-rich shell (Figure 8a) and (2) larger particles consisting almost completely of Pt, with internal pores from the removed Cu (Figure 8b). At GM, correlations of ORR activities with relative populations of the two particle types in different samples suggest that the core–shell particles provide most of the activity. However, for similar structural observations in the PtCo system, the group of Yang Shao-Horn has raised the point that much of the enhanced activity might arise from the latter type of particles due to exposure of additional Pt area with particular densities of monatomic steps, which the group of Juan Feliu, working with stepped pure-Pt single crystals, found to have higher specific activity.45 Continuing work in this area seeks to determine (1) just how deeply beneath the surface an alloying atom can be and still contribute to enhanced activity and (2) the relative contributions of ligand i.e., nearby alloying element atom) effects versus lattice compression effects to the enhanced activity. Much more work is also needed on the durability of partially dealloyed catalysts.

The dealloyed catalyst effect may be more general than recent literature suggests. Earlier reports from the Watanabe group showed enhanced activity for catalysts from which most if not all alloying element atoms were removed from the top several atomic layers by voltage cycling in aqueous acid (as confirmed by X-ray photoemission spectroscopy),
leaving what they called a “Pt-skin” layer. Anomalously low absolute ORR activities reported for pure Pt electrodes in ref 47 have lessened its impact on the field, thereby pointing out the need for frequent rechecks of the absolute mass activity of baseline Pt/C catalysts in all ORR research. The Watanabe “Pt-skin” layer is equivalent to what single-crystal electrochemists have more recently called “Pt-skeleton” electrodes; in this literature, the “Pt-skin” term refers to single monolayers of Pt segregated to the surface of alloys by thermal annealing, which showed higher activity than rougher Pt-only “skeleton” surfaces produced by acid dissolution. It is possible that high-activity outliers in testing of “normal” alloys have arisen from particular processing conditions leading to advantageous (and adventitious?) dealloyed configurations.

Monolayer Catalysts: Since in typical Pt/C catalysts about one-fourth of the Pt atoms reside on the surfaces of particles, replacement of all nonsurface atoms by something other than Pt could improve Pt mass activities by a factor of 4, assuming no change in area-specific activity. Radoslav Adzic and co-workers have worked out techniques to coat controlled thicknesses of one or several monolayers of Pt or Pt alloys onto non-Pt cores. In rotating disk electrode experiments, they found such catalysts to give ORR Pt mass activities up to ~10 times that of standard Pt/C, achieving increases in area-specific activities as well. However, the cores found to be workable to date have contained large amounts of other noble metals, and the best activities to date, normalized to the mass of the total noble metal mass, are only about 3-fold higher than those of Pt/C. Most of the other PGMs that can be used in cores, due to their relative scarcity versus Pt, would have their prices rise to well above that of Pt if used in any quantity. Of the other PGMs, palladium is the most plausible in this regard, and PtML/Pd core catalysts would presently have a significant price advantage over pure Pt. However, even Pd was more costly than Pt in 2000–2001 after it replaced much of the Pt in automotive catalytic converters and before, in response to the price rise, other uses of Pt were shifted to alternative materials. Any breaks in the Pt monolayer, exposing Pd, could be expected to lead to durability problems both at ORR potentials (dissolution of Pd followed by redeposition at lower potentials of Pd on Pt, poisoning the ORR) and at the hydrogen potentials that the cathode might see at shutdown (fracturing due to repeated formation and decomposition of Pd hydrides). Further research in monolayer catalysts is needed to (1) develop workable core materials containing at most a few percent noble metal, (2) develop improved deposition techniques to increase the uniformity of the deposited monolayer, and (3) make extended MEA-based tests of durability in this catalytic system in which dissolution of a single monolayer of Pt could completely deactivate the catalyst.

Controlled Crystal Face Orientation Catalysts: Experiments at Lawrence Berkeley and Argonne National Laboratories with ~6 mm diameter single-crystal surfaces of pure Pt have shown ORR activities for the (111), (100), and (110) faces all within a factor of 2 of each other (Table 3) and all within a factor of 2 of a polycrystalline Pt disk (~10 times the specific activity of Pt/C). ORR on pure Pt therefore seems relatively insensitive to crystal face orientation, but the situation can be quite different on Pt alloys.

Table 3. ORR Activities for Different Crystal Faces of Pt and Pt3Ni

<table>
<thead>
<tr>
<th>crystal face</th>
<th>Pt μA/cm² @900 mV</th>
<th>Pt3Ni μA/cm² @900 mV</th>
<th>Pt3Ni/Pt activity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>2200</td>
<td>5100</td>
<td>2.3</td>
</tr>
<tr>
<td>(100)</td>
<td>900</td>
<td>2200</td>
<td>2.4</td>
</tr>
<tr>
<td>(111)</td>
<td>1900</td>
<td>18000</td>
<td>9.5</td>
</tr>
</tbody>
</table>

*Data from ref 51, with missing y-axis numbers filled in from Ross, P. N.; Markovic, N.; Stamenkovic, V.; Blizanac, B. DOE Hydrogen/Fuel Cell Program Annual Review 2006, Project FC-10.*

While (100) and (110) surfaces of Pt3Ni gave the normal alloy activity multiplier of ~2 versus the equivalent pure Pt surfaces, the (111) face of Pt3Ni, with a monolayer of Pt thermally segregated to the surface, showed ~10 times the activity of Pt(111), that is, a 5-fold additional structure-dependent activity enhancement, giving an overall specific activity 90 times that of commercial Pt/C. If one could achieve the 18000 μA/cm² specific activity @ 900 mV of Pt3Ni(111) (measured by RDE, without cell resistance correction) in a fuel cell, one would need a surface area of only 6 m²/g Pt to achieve the 8× mass activity improvement target. Motivated by these results, several research teams are working on growing Pt alloy nanoparticles with a high fraction of their surface areas in the form of {111} facets. The group of Hong Yang at the University of Rochester has grown ~6 nm Pt3Ni catalysts having controlled mixtures of truncated octahedra (exposing {111} and {100} facets) and cubes (exposing only {100} facets). Figure 9 shows that ORR activity measurements by RDE at GM showed a linear increase in ORR activity with the fraction of the total area in {111} facets, and extrapolation of the data yields a {111}/[100] activity ratio of 4, compared to 8 for large single crystals. James Fang and the group at SUNY Binghamton have grown ~11 nm Pt3Ni octahedra (only {111} facets) (Figure 10a) and cubes, for which Shouzhong Zou and group at Miami University (Ohio) measured a {111}/[100] activity ratio of 5 (Figure 10b). While the observation of {111} enhancement of ORR activity in practically sized Pt alloy nanoparticles is encouraging, the absolute specific activities for {111} facets measured by both groups is still a factor of 10–20 lower than the activity previously reported for large single-crystal surfaces. This activity shortfall may be due to very small facet sizes, to residual point defects (adatoms or vacancies) within the facets, to incomplete segregation of Pt to the surface, or (in some cases) to residues of the surfactants used to control the crystal face during growth. Continuing work, both with
nanoparticles and with stepped large single crystals, will determine whether the very high activities reported for large Pt₃Ni\(\{111\}\) faces can be successfully harvested in practical catalysts.

One might doubt the durability of catalysts dependent upon one particular near-perfect surface structure to yield surprisingly high specific activities. However, the cyclic voltammograms of \(\{111\}\) surfaces of both Pt and Pt₃Ni (Figure 11) show unusually reversible oxygen electro sorption/electrodesorption peaks in the 0.6–1.0 V RHE operating range of a fuel cell. This reversibility suggests that the oxygen species is adsorbed on top of the Pt surface. In contrast, polycrystalline Pt and Pt alloys and other crystal faces show highly irreversible surface redox peaks in this voltage range (which is relevant to vehicular fuel cell operation). This irreversibility has been ascribed to place exchange, whereby O atoms move beneath the initial Pt surface and some Pt atoms move up.\(^{54}\) When such a place-exchanged oxide layer is reduced, the removal of oxygen atoms causes Pt atoms to move. A small fraction of the moving Pt atoms dissolves into the electrolyte phase and can be transported to neighboring Pt particles (electrochemical Ostwald ripening) or to elsewhere in the fuel cells, where they can deposit partway through the membrane where an excess of local dissolved H₂ over dissolved O₂ first produces local reducing conditions. This mechanism is thought to be a major contributor to the loss of surface area and ORR activity in Pt/C electrocatalysts under automotive-relevant load cycling. While the activity of \(\{111\}\) faces may be highly sensitive to changes in local structure, the suppression of place exchange to higher potentials on \(\{111\}\) may provide the structural stability needed to maintain the very high activity. With such questions to be investigated, these are exciting times indeed in the world of electrochemical surface science!

Non-Pt Catalysts: The holy grail of electrocatalytic research has been a noble-metal-free ORR catalyst active and durable in acid electrolytes. In alkaline solution, where a broader range of materials is stable against corrosion and the electrocatalysis is easier, suitable non-Pt catalysts are already available. However, at least until \(\text{OH}^-\)-conducting ionomers with ionic conductivities similar to perfluorosulfonic acid polymers are available, alkaline fuel cells will use aqueous electrolytes and face current density limitations intrinsic to flooded electrodes. Even if this problem can be fixed, the alkaline fuel cell generates its product water on the anode, where there is no unreacted nitrogen flow to push water droplets out of the way as there is for the air-fed cathode of an acid polymer electrolyte fuel cell.

Non-Pt ORR catalysts for use in acid have evolved over time from hemoglobin analogue macromolecules to metalized, nitrogen-derivatized carbons that can pack many more active sites into a given volume. This site density, multiplied by the turnover frequency of each site, sets the critical factor in assessing the activity of a catalyst that is essentially cost-free, A/cm² of catalyst.\(^{34}\) A/mg does not matter when one’s materials are 10²–10⁴-fold cheaper than Pt; one simply needs to be able to pack enough catalyst into the volume available for the fuel cell without using electrodes so thick as to be choked off by mass-transport considerations. The initial ORR activity goal set by DOE (on the assumption that good electrodes can be made at least 100 μm thick) of 130 A/cm² has now been essentially met, at very low current densities in 1 cm² (Figure 12b) and in 50 cm² fuel cells at GM, by non-Pt catalysts from the group of Jean-Pol Dodelet at INRS.\(^{55}\) (Figure 12), and substantial progress is also being

![Figure 9](image1.png)

**Figure 9.** Pt mass- and Pt area-specific ORR activities in 0.1 M HClO₄ at 25 °C as a function of the fraction of the total surface in \(\{111\}\) facets for Pt₃Ni in the form of varying mixtures of cubes and truncated octahedral. Reproduced from ref 52 with permission from the American Chemical Society.

![Figure 10](image2.png)

**Figure 10.** (a) Scanning electron micrograph of Pt₃Ni nanooctahedra. (b) Pt mass- and Pt area-specific activities by RDE in 0.1 M HClO₄ for Pt₃Ni octahedra and cubes and for Pt cubes. Reprinted from ref 53 with permission from the American Chemical Society.
made at Los Alamos National Lab by Piotr Zelenay and co-workers.\textsuperscript{56}

However, breakthroughs are still needed in durability and in mass transport. LANL has shown durability into hundreds of hours,\textsuperscript{57} but this was at potentials much lower than the 600 mV RHE, which is the minimum (at full power) to allow adequate heat rejection for automotive use. The durabilities of these types of catalysts have decreased greatly while drawing current at potentials higher than those used in the LANL test. To date, the ∼100 μm thick non-Pt electrodes needed to achieve kinetic-region current densities equivalent to those of 10 μm Pt/C electrodes cannot support anything like the 1.5 A/cm$^2$ needed for an automotive fuel cell. Non-Pt catalyst research needs to move on from a focus on pure kinetic activity to address these two other still-daunting problems.

Performance Falloff at High Current Densities for Low-Loaded Cathodes: So far, the fuel cell discussion in this paper has focused on kinetic ORR activity as measured at low current densities in H$_2$/O$_2$ fuel cells, the major factor determining fuel economy at highway cruise conditions. However, for automotive applications, the ability of a catalyst to deliver at least 1.5 A/cm$^2$geo at potentials above 0.6 V RHE in a H$_2$–air fuel cell is also critical primarily to limit the amount of heat that must be rejected at high power, though also for considerations of fuel economy. While such performance is being routinely achieved for standard dispersed Pt/C catalysts at cathode loadings of 0.4 mgPt/cm$^2$, as one repeatedly halves the Pt loading for such catalysts, one does not simply depress the whole H$_2$–air polarization curve by 20 mV at each step (as one would expect from simple kinetics with the 70 mV/decade Tafel slope measured for 0.4 mgPt/cm$^2$ Pt/C in H$_2$/O$_2$ fuel cells up to 2 A/cm$^2$).\textsuperscript{34} Rather, the performance at higher current densities gets progressively worse as the Pt loading is decreased.\textsuperscript{58} The discrepancy between measured and expected behavior does not get any better if the data are corrected for known transport losses (membrane and electrode hydrogen ion resistances and oxygen-transport resistances), which scale with the geometric area of the electrode (Figure 13a). The membrane ionic resistance was derived from high-frequency resistance measurements. Electrode ion resistance was obtained by applying a one-dimensional model to AC impedance data. Gas-transport resistances through the diffusion media were modeled with Stefan-Maxwell equations utilizing effective diffusion coefficients, and gas transport through the electrode was modeled as Fickian diffusion with an effective diffusion coefficient.

However, if one replots the data using as the x-axis not the conventional geometric current density but rather the current density per active Pt surface area (measured by hydrogen electrosorption), the data for different Pt loadings superimpose (Figure 13b). This observation suggests that whatever is restricting the high current density performance is happening at or very close to the surface of each Pt nanoparticle, either a kinetic phenomenon or as a very local transport restriction. None of the already-proposed complications to ORR kinetics,\textsuperscript{51} with modification. Reprinted with permission from AAAS, copyright 2007.

Figure 11. Cyclic voltammograms for Pt and Pt$_3$Ni (111) surfaces showing reversibility of initial oxidation region below 1 V RHE. From ref 51, with modification. Reprinted with permission from AAAS, copyright 2007.

Figure 12. (a) Schematic of the proposed active site of active non-Pt ORR catalysts from INRS. (b) The 1 cm$^2$ H$_2$/O$_2$ fuel cell data at 80 °C, showing equivalent initial activity at 0.9 V RHE for a ∼100 μm thick non-Pt catalyst and a commercial (∼10 μm-thick) Pt/C-catalyzed cathode. For non-Pt catalysts, falloff at higher current densities exemplifies remaining challenges on mass transport. From ref 55. Reprinted with permission from AAAS, copyright 2009.
such as a doubling of Tafel slope at low potentials where the Pt surface is oxide-free, can generate losses as large as those observed. To explain the losses as a pure transport phenomenon, the assumption of bulk diffusivities requires thicknesses of transport-restricting materials such as ionomer or water that are at least an order of magnitude thicker than seems geometrically possible. Alternatively, one would have to propose oxygen diffusivities through nm-thick films which are orders of magnitude smaller than those for bulk materials, a physically implausible condition. That this kind of local current density dependent falloff is seen for conventional carbon-supported electrodes but not for some alternate electrode structures gives hopes for improved understanding and ultimate solution to enable the higher area-specific kinetic activity being developed now to find practical applications in fuel cells. The high current density, low-loaded falloff is thus a challenge worthy of the attention of the best chemical engineering talent.

Overall Comparison between Battery and Fuel Cell Systems. If the range problems of batteries could be solved, the pathways to acceptably low fuel cell Pt usage could be brought to fruition, and hydrogen and electrical infrastructure issues could adequately be addressed; the choice between these two technologies for electrification of the automobile would come down to matters of the overall system and lifetime operating costs. Li ion batteries use intrinsically cheap materials but require a very large surface area of very finely controlled thin layers, interfaces, and separators and, by their nature, use monopolar design (current collectors coming out of the side of each cell). Li ion batteries are already mass-produced for use in portable electronic devices; therefore, many of the opportunities for cost reduction through scale have already been taken, and therefore, cost reduction must be addressed through the development and implementation of improved materials. Fuel cells utilize some intrinsically more-expensive materials, though as we have seen, pathways exist for drastic reductions in the amounts used. Due to the much higher current densities obtainable with the more conductive fuel cell electrolyte, the total geometric surface area of the cells is ~30-fold less. The ability to use bipolar construction, with cells stacked in series with the negative current collector of one cell serving also as the positive current collector of the adjacent cell, further simplifies the structures. However, fuel cell systems also require more complex balance of plant, including a hydrogen tank and an air compressor. In summary, ongoing development work should be coupled to continued reevaluation of the system-level physical feasibility and relative cost structures of BEV and FCEV systems, with the results informing future strategy setting.

Both Li ion battery electric vehicles and fuel cell vehicles warrant continued strong development investment, given the strong societal need for full vehicle electrification and the large risk that either path will achieve high-volume commercial cost targets. One plausible scenario is that both technologies will have a place in the automotive future, with batteries finding theirs in smaller cars for short trips, while fuel cells find application in larger vehicles used regularly for longer trips. Critical technical development needs to continue, with thoughtfully weighted targeting in both areas to overcome well-identified shortcomings of these electrochemical technologies. Those exploring the fascinating scientific details in these dynamic areas of electrochemistry can broaden their impact by keeping a careful eye on ultimate system-level benefits of their work.

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REFERENCES


PERSPECTIVE


