Lithium-Ion Batteries: Possible Materials Issues

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Abstract

The transition to plug-in hybrid vehicles and possibly pure battery electric vehicles will depend on the successful development of lithium-ion batteries. But, in addition to issues that affect performance and safety, there could be issues associated with materials. Many cathode materials are possible, with trade-offs among cost, safety, and performance. Oxides of cobalt, nickel, manganese, and aluminum in various combinations could be used, as could iron phosphates. The anode material of choice has been graphite, but titanates may be used in the future. Similarly, different materials could be used for other parts of the cell. We consider four likely battery chemistries and estimate the quantities of all of these materials that could be required if vehicles with large batteries made significant market inroads, and we compare these quantities to world production and resources to identify possible constraints. We identify principal producing countries to identify potential dependencies on unstable regions or cartel behavior by key producers. We also estimate the quantities of the materials that could be recovered by recycling to alleviate virgin material supply restrictions and associated price increases.

1. Introduction

As the world energy community evaluates alternatives to petroleum for personal vehicles, every aspect of potentially important technologies must come under intense scrutiny. Technical and economic issues receive most of the attention, but material availability is important to consider whenever rapid growth is expected — or even encouraged. Lithium-ion batteries are a very promising contributor to reducing our dependence on imported oil. But is there enough lithium? Will we need to import it from a new and unfriendly cartel? What about other battery materials? The adequacy of lithium supply for a large battery industry was recently questioned by Tahil (2007, 2008), but his conclusions were disputed by Evans (2008). In this paper, we explore the potential demand for lithium and other key battery materials if hybrids, then plug-in hybrids, and then pure electric vehicles expand their market share extremely rapidly[1]. This is not meant to be a projection, but rather an upper bound on the quantity of material that could be required. The total demand can then be compared to estimates of production and reserves to evaluate the adequacy of future supply. Note that for this paper, demand has been estimated for U.S.

[1] We will refer to all three types as electric vehicles, or vehicles with electric drive.

vehicle use only; world demand, including that for all other battery applications, must eventually be included as well.

Several steps are required to estimate total U.S. demand for materials. These are listed below.

- Estimate total vehicle demand vs. time
- Estimate percent of new sales by each technology vs. time
- Calculate the number of new vehicles by type annually
- Design appropriate batteries for each vehicle type and for each chemistry
- Determine percent of lithium (or cobalt, nickel, etc.) in each active material and then the battery pack
- Estimate battery mass for each vehicle type
- Estimate total lithium required, by year, for each chemistry
- Estimate demand for other materials
- Estimate materials available for recycling vs. time
- Estimate net virgin material required
- Compare to production and reserves

2. Vehicle Demand

For its Annual Energy Outlook 2008, the Energy Information Administration (EIA) projected light vehicle sales for the United States to 2030 . Assumptions behind the EIA's transportation projections can be found on the EIA website (EIA 2008). Argonne staff extended these projections to 2050 by using a model based on Gross Domestic Product (GDP), fuel price, and projections of driving-age population. This extension was performed for the VISION 2007 model (2007).

As can be seen in Figure 1, only moderate growth is projected between now and 2050, and most of that growth is expected in the light truck market, which sees over a 50% growth in sales, while the passenger automobile market is almost stagnant.

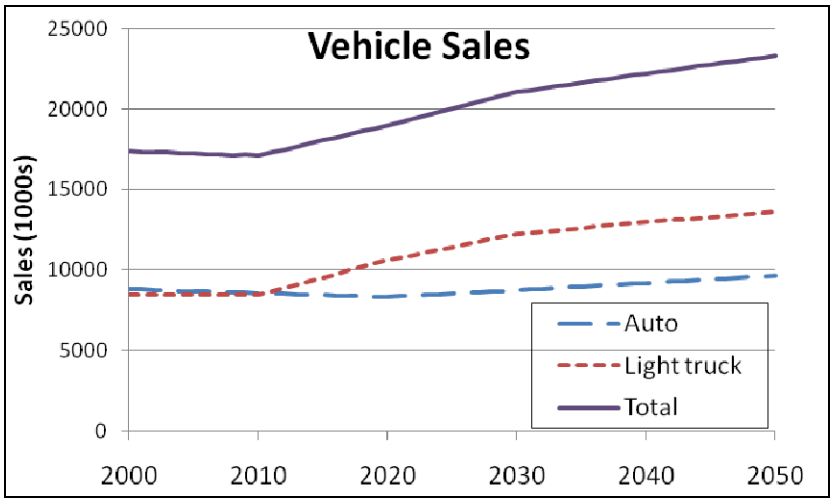

Figure 1 U.S. Light-Duty Vehicle Sales Projection to 2050

Next, we took the most optimistic scenario for penetration of vehicles with electric drive into the U.S. market from the DOE Multi-Path Study (Phase 1) (DOE 2007). In this scenario, 90% of all light-duty vehicle sales are some type of electric vehicle by 2050 (see Figure 2). This is an extreme case scenario**,** not a projection**.** It represents the maximum percent of U.S. sales that could be accounted for by hybrid vehicles like those on the road today (HEV), plug-in hybrids with different all-electric ranges (PHEVX, where X is the all-electric range in miles), and pure electric vehicles (EVs). Plug-in hybrids are generally assumed to operate in all-electric or charge-depleting mode for the first X miles of travel, but then they run as a conventional hybrid in charge-sustaining mode when the battery state-of-charge declines to a predetermined percentage. In reality, operation in blended mode, where the engine could supply peak power during the "electric" miles, would be more efficient and allow designs with smaller and more economical batteries.

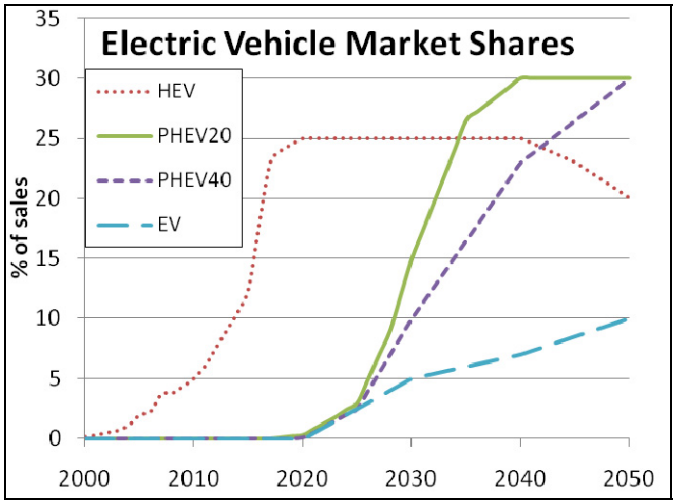

Figure 2 Optimistic Scenario of Electric Vehicle Market Shares

We interpolated both the total vehicle sales for passenger cars and light trucks (Figure 1) and the market shares of electric vehicle types from the Multipath Study (Figure 2) and combined them in an Excel spreadsheet to yield total numbers of vehicles sold of each type in each year, as can be seen in Figure 3. The maximum total annual sales of vehicles with electric drive occur in 2050, when they have grown to 21 million units, of which plug-in light trucks represent over 8 million units.

In this scenario, sales of PHEVs are beginning to plateau, but sales of EVs are advancing, accounting for about 2.4 million new vehicles in 2050. The actual penetration of EVs will be seen as a key factor in material demand, because these vehicles require larger batteries. The cumulative total for sales of all types of electric vehicle in the United States until 2050 is 465 million vehicles.

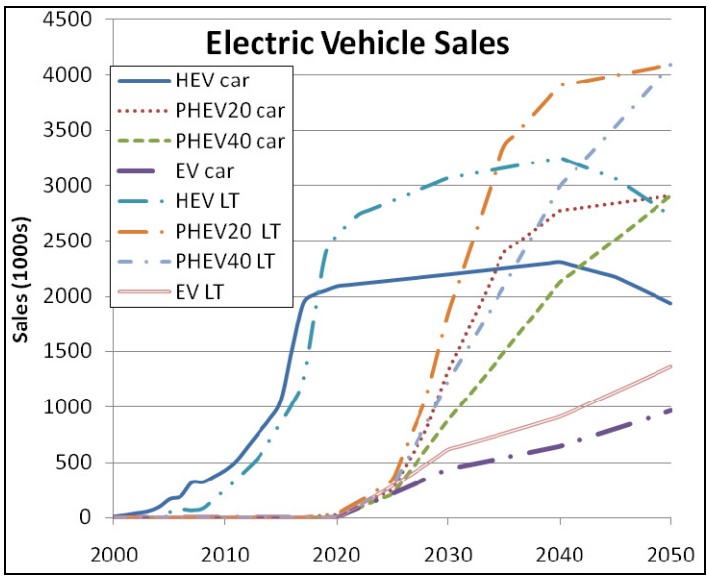

Figure 3 U.S. Electric Vehicle Sales by Type, to 2050

3. Batteries

Next, we needed to characterize the batteries so that we could estimate how much material would be required for each type of vehicle and then for the United States as a whole. Although the dominant chemistry used in electronics batteries today uses a mixture of nickel, cobalt, and aluminum (NCA) for the lithium salt in the active material for the cathode (positive electrode), numerous other materials are serious contenders for automotive batteries. Each has advantages and disadvantages that could eventually lead to any of these becoming the major material used. We chose three promising chemistries, in addition to the current NCA-Graphite, to compare on the basis of material usage. These are defined in Table 1. All contain lithium in a salt for the cathode active material, and all contain a lithium salt ($LiPF_6$) in the electrolyte solution as well. One also uses a lithium titanate salt, instead of the standard graphite, in the anode. For each battery chemistry analyzed, all materials in the electrodes and the electrolyte were tabulated to give total material required.

Table 1 Battery Chemistries Included in the Analysis

System Electrodes	NCA Graphite	LFP (phosphate) Graphite	MS (spinel) Graphite	MS TiO
Positive (cathode)	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	$LiFePO_4$	$LiMn_2O_4$	$LiMn_2O_4$
Negative (anode)	Graphite	Graphite	Graphite	$Li_4Ti_5O_{12}$

The actual chemical formulae were used to obtain elemental percents by weight in the active compounds, as can be seen in Table 2. For NCA-G, Li can be seen to be 6.94/96.08, or 7.2% by mass of cathode active material.

Table 2 Mass of Elements in Active Compounds

	Mass	Number per Molecule				
Element	AMU	NCA	LFP	MS	TiO	$LiPF_6$
Li	6.94	1	1	1	4	1
Ni	58.69	0.8	0	0	0	0
Co	58.93	0.15	0	0	0	0
Al	26.98	0.05	0	0	0	0
O	16	2	4	4	12	0
Fe	55.85	0	1	0	0	0
P	30.97	0	1	0	0	1
Mn	54.94	0	0	2	0	0
Ti	47.88	0	0	0	5	0
F	19	0	0	0	0	6
Total Mass (AMU)		96.08	157.76	180.82	459.16	151.91

Four batteries were designed — one for each of the chemistries chosen — for each of three automobile all-electric ranges (a standard hybrid was simulated as a PHEV4). Battery designs assumed blended-mode operation. Table 3 shows a partial breakdown of the material masses per cell. The table also shows total cell mass and numbers of cells required for each of the 12 cases.

From (1) the mass percent of each element in the active compounds and (2) the mass required of each compound in the batteries, we calculated the quantities of lithium and other materials required per battery pack. For lithium, the total is the sum of lithium from the cathode, the electrolyte, and the

anode (for the cells with titanate anodes). The total requirement of lithium (on an elemental basis) for each car is shown in Table 4. The electric vehicle battery requirement is based on an assumed 100-mile range. A longer range would increase both the material required and the cost to the extent that significant market penetration is unlikely. Results from other analyses, such as Tahil's, project higher demand, on the basis of assumed higher EV range. Our colleagues, who have investigated market potential of electric drive, find that the benefit-to-cost ratio of added all-electric range for vehicles with electric drive drops very rapidly, casting doubt on the marketability of EVs with ranges greater than 100 miles (Santini et al. 2009). However, if range is dropped well below 100 miles in "city electrics" to save on electric vehicle cost, then market share is estimated to drop because such vehicles meet the needs of few customers (Vyas et al. 2009). Such deductions suggest that less "EV-optimistic" scenarios are more credible.

Table 3 Detailed Automobile Battery Composition

	Battery Type											
Parameter	**NCA-G**			**LFP-G**			**LMO-TiO**			**LMO-G**		
Vehicle Range (mi) at 300 Wh/mile	**4**	**20**	**40**	**4**	**20**	**40**	**4**	**20**	**40**	**4**	**20**	**40**
Materials Composition (g/cell)												
Cathode (+) active material	**77**	**314**	**635**	**74**	**302**	**609**	**125**	**502**	**1,003**	**63**	**255**	**514**
Anode (-) active material	**51**	**209**	**423**	**51**	**208**	**419**	**83**	**334**	**669**	**42**	**170**	**342**
Electrolyte	**50**	**149**	**287**	**64**	**194**	**376**	**69**	**239**	**477**	**41**	**124**	**242**
Total cell mass (g)	**424**	**1,088**	**2,043**	**471**	**1,162**	**2,170**	**483**	**1,534**	**3,062**	**347**	**888**	**1,671**
Cells per battery pack	**60**	**60**	**60**	**60**	**60**	**60**	**60**	**60**	**60**	**60**	**60**	**60**
Battery mass (kg)	**31.2**	**75.9**	**140.1**	**34.6**	**81.6**	**150.2**	**35.6**	**106.2**	**209.1**	**26.1**	**62.6**	**115.4**

Table 4 Total Lithium Required per Passenger Automobile

	Battery Type															
Parameter	**NCA-G**				**LFP-G**				**LMO-G**				**LMO-TiO**			
Vehicle range (mi) at 300 Wh/mile	4	20	40	100	4	20	40	100	4	20	40	100	4	20	40	100
Vehicle type	HEV	PHEV	PHEV	EV	HEV	PHEV	PHEV	EV	HEV	PHEV	PHEV	EV	HEV	PHEV	PHEV	EV
Li in cathode (kg)	0.335	1.36	2.75	6.88	0.196	0.796	1.61	4.02	0.145	0.587	1.18	2.96	0.287	1.165	2.31	5.78
Li in electrolyte (kg)	0.035	0.104	0.202	.505	0.045	0.136	0.264	.528	0.029	0.087	0.170	.425	0.049	0.167	0.335	.838
Li in anode (kg)	0	0	0	0	0	0	0	0	0	0	0	0	0.301	1.21	2.43	6.07
Total Li in battery pack (kg)	0.370	1.46	2.96	7.39	0.241	0.932	1.87	4.68	0.173	0.674	1.35	3.38	0.637	2.54	5.07	12.68

Battery (and material) masses were scaled up from the designs for automobiles to ones that would be appropriate for light trucks or sport utility vehicles (SUVs), on the basis of computer runs using the Powertrain Systems Analysis Toolkit (PSAT) model (PSAT 2009), for the Multi-Path Study (Plotkin and Singh 2008). This is not a simple linear scale-up from the automobile masses because of the different performance features required by the different vehicle types. The battery mass for PHEV20 light trucks was estimated from Table 5 by interpolation of the PHEV10 and PHEV40 ratios of SUV battery mass to car battery mass, which are actually not very different. Similarly, 2050 ratios were obtained by extrapolation from 2045.

Table 5 Relative Battery Masses for Cars and Light Trucks (kg/vehicle)(Plotkin and Singh 2008)

	Mass, by Type			
Vehicle Category	**HEV**	**PHEV10**	**PHEV40**	**EV**
MID-SIZE CAR				
2015	34	46.6	92.6	316
2030	31	42.8	84.2	279
2045	32	41.3	81.7	267
MID-SIZE SUV				
2015	40	56.2	119.7	431
2030	37	52	110.8	395
2045	37	50.9	107.6	380

4. Total Lithium Requirements

Once the total quantities of material required per vehicle by type were determined, they could be multiplied by the annual numbers of vehicles by type to provide an estimate of the material demanded by year. Figure 4 shows the result for lithium, assuming that all vehicles used the current NCA-Graphite chemistry. The demand is seen to rise to over 50,000 metric tons annually by 2050. The demand for lithium for PHEV40 light trucks is largest by 2030, with all-electric light truck material demand second by 2040. Material demand for HEVs is almost negligible. Similar results were obtained for the other chemistries analyzed.

Next, we compared U.S. auto battery demand to world production. Future work must, of course, add demand from the rest of the world to this analysis. Figure 4 also shows how potential U.S. lithium demand compares to historical world production and U.S. consumption. The U.S. consumption is perhaps misleading, since it only accounts for direct purchases of lithium compounds by U.S. firms and omits indirect consumption in the form of imported batteries and products containing batteries. If large numbers of batteries were ever produced in the United States, the consumption curve would then reflect more realistic usage. Note that demand for lithium for automotive batteries has a very long way to go before it strains current production levels, with U.S. demand, even under this aggressive penetration scenario, not reaching current production levels until after 2030. Even if world demand were four times U.S. demand, current production levels would be sufficient to cover automotive battery demand (only) until about 2025. It is reasonable to expect the lithium production industry to be able to expand at the relatively slow rate required to meet automotive battery demand.

We then considered the potential impact of recycling on net demand for materials. Figure 4 also shows the demand curve lagged by 10 years (assumed average battery life) to approximate material that would be available for recycling if all lithium were recycled. The effect of less-optimistic assumptions and a more realistic vehicle survival function will be included in future work. Finally, the graph shows the difference between the gross material demand and the potentially recyclable material. This represents the net quantity of virgin material that would be required if all battery material could be recycled. Note that this curve turns over, meaning that the quantity of virgin material required actually declines after about 2035, having reached a maximum of about 20,000 metric tons per year, just under current production levels. The net demand turns around because the rate of demand growth slows.

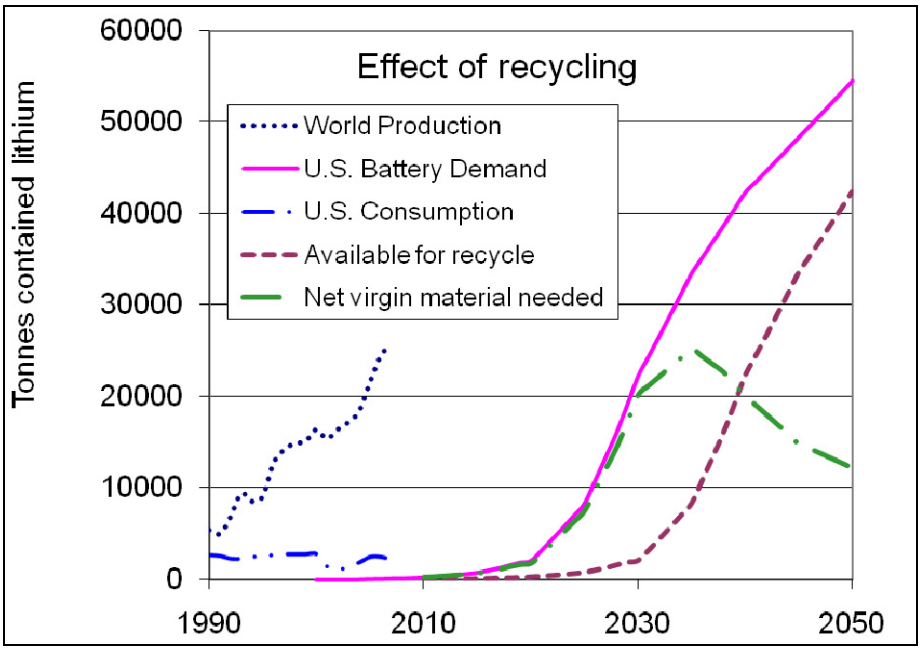

Figure 4 Future U.S. Lithium Demand Compared to Historical Production

Of course, demand for lithium for electronics batteries — which currently makes up essentially all battery demand for lithium — must be projected forward and included. This remains to be done. Figure 5 shows that battery demand currently accounts for about 25% of world lithium production. However, batteries are by far the fastest growing use, and so future lithium demand is likely to be dominated by batteries.

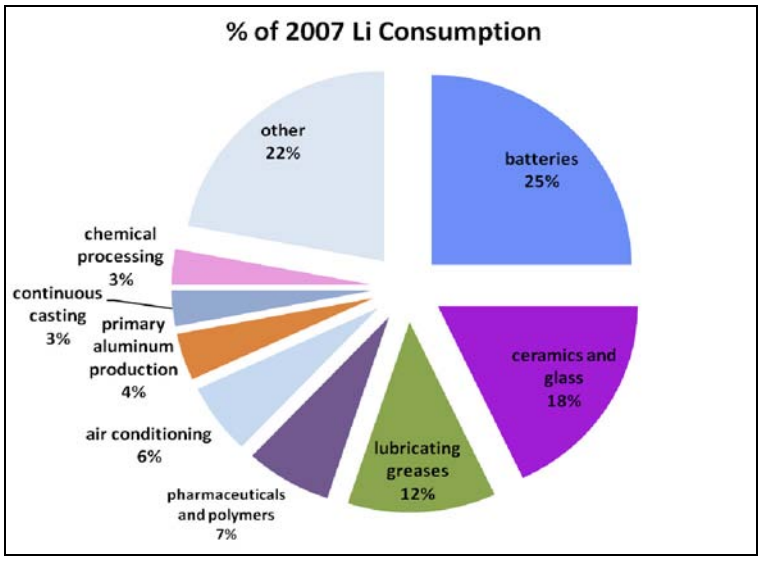

Figure 5 Current World Lithium Markets (USGS 2008a)

We also estimated cumulative battery demand for lithium and other materials for light-vehicle batteries, under the assumption that 100% of all batteries were produced from only one chemistry. Total (gross) potential lithium demand for the four chemistries is shown in Figure 6. (This was done for each of the four chemistries in turn, so the total demand numbers should not be added.) This total was then compared to United States Geological Survey (USGS) estimates of the world reserve base, which are considerably lower than recent estimates by experts (Evans 2008). USGS estimates are shown in Table 6. The maximum demand would occur if all batteries were made by using titanate anodes, since this chemistry uses the most lithium per battery. But even in that case, total demand is about 1.8 million metric tons, compared to world reserves and reserve base of 4 and 11 million metric tons, respectively. (The USGS definitions of reserve and reserve base are provided in the Appendix.) Even when our U.S. estimates are multiplied by a factor of 4 to account for world demand, it appears that there is enough lithium available to use while we work toward an even more efficient, clean, and abundant means of supplying propulsion energy.

Table 6 also lists the locations of current lithium production and known reserves. Chile dominates current production, with Australia second. Bolivia has huge untapped reserves, and China is rapidly developing its production capacity. The United States has very limited reserves, and so it is likely to always be a materials importer, although batteries could certainly be produced here from these imported materials. The United States has relatively stable relationships with the major lithium-producing countries, and so significant supply problems are not anticipated at present.

Table 6 Lithium Production and Reserve Statistics (adapted from USGS 2008b)

World Mine Production, Reserves,[a] and Reserve Base[a]:				
	Mine production		**Reserves**	**Reserve base**
	2006	**2007[e]**		
United States	W	W	38,000	410,000
Argentina[e]	2,900	3,000	NA	NA
Australia[e]	5,500	5,500	160,000	260,000
Bolivia	—	—	—	5,400,000
Brazil	242	240	190,000	910,000
Canada	707	710	180,000	360,000
Chile	8,200	9,400	3,000,000	3,000,000
China	2,820	3,000	540,000	1,100,000
Portugal	320	320	NA	NA
Russia	2,200	2,200	NA	NA
Zimbabwe	600	600	23,000	27,000
World total (rounded)	23,500	25,000	4,100,000	11,000,000

[a] See Appendix for definitions
[e] Estimated

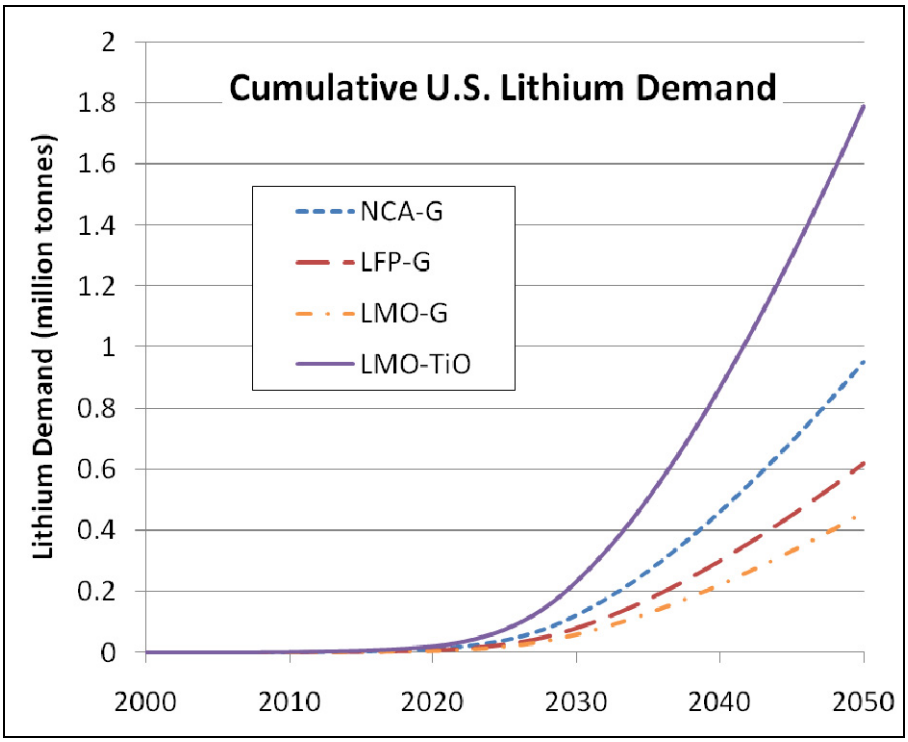

Figure 6 Cumulative U.S. Lithium Demand for Four Battery Chemistries

5. Other Materials

We also estimated cumulative demand for other materials that could be required for electrodes of lithium-ion batteries. Using the same scenario and methods described earlier for lithium, we prepared the potential demand for nickel, cobalt, and aluminum for NCA-graphite batteries; iron and phosphorus for LFP batteries; manganese for either the LMO-G or LMO-G; and titanium for the LMO-TiO. Figure 7 shows the cumulative demand for these materials, again assuming that all U.S. light-duty electric vehicle batteries were made by using only the chemistry requiring the material.

These quantities were then compared to USGS reserve data for each material, if appropriate. For some materials, such as iron, the quantity available is sufficiently large that another measure was used for comparison. Table 7 compares material availability to potential cumulative U.S. light-duty battery demand to 2050 and estimates the percent that could be required. A potential constraint was identified for one material. If NCA-G were the only chemistry used, cobalt use could make a dent in the reserve base by 2050. Approximately 9% of the world reserve base could be required by 2050 for U.S. light-duty vehicle batteries. Of course, recycling — which is more likely with an expensive, scarce material — would significantly alleviate this pressure.

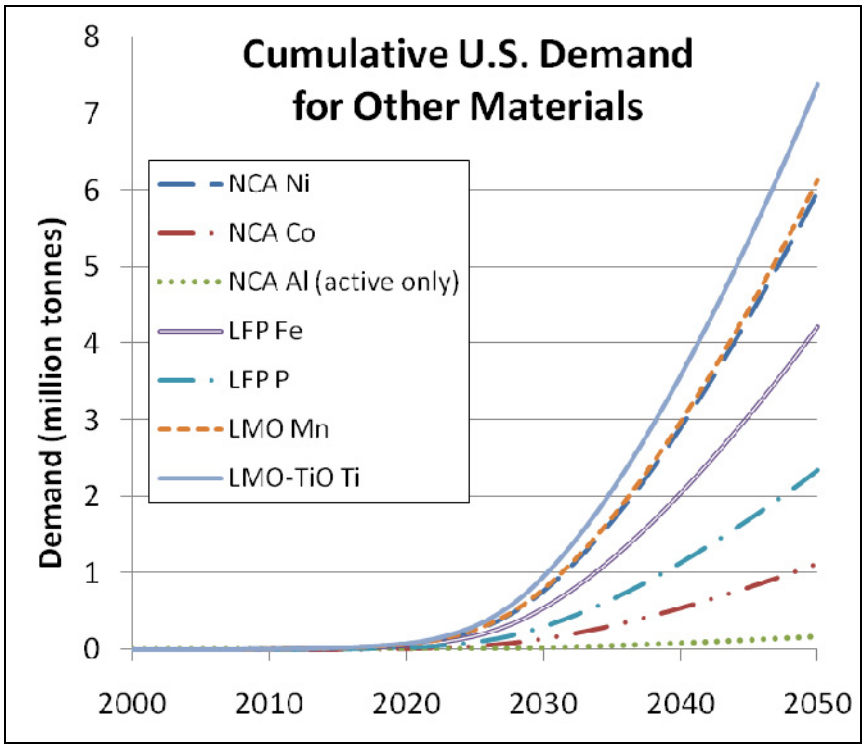

Figure 7 Cumulative U.S. Demand for Other Battery Materials

Table 7 Comparison of U.S. Light-Duty Battery Demand to Material Availability

Material	Availability (million tons)	Cumulative Demand	Percent Demanded	Basis
Co	13	1.1	9	World reserve base
Ni	150	6	4	World reserve base
Al	42.7	0.2	0.5	U.S. capacity
Iron/steel	1320	4	0.3	U.S. production
P	50,000	2.3	~0	U.S. phosphate rock production
Mn	5200	6.1	0.12	World reserve base
Ti	5000	7.4	0.15	World reserve base

The United States does not produce any cobalt, and so we must depend entirely on imports[2]. In 2006, "ten countries supplied more than 90% of US imports. Russia was the leading supplier, followed by Norway, China, Canada, Finland, Zambia, Belgium, Australia, Brazil, and Morocco (USGS 2008c)." Cobalt is produced in many other countries as well, so it is unlikely that any one country or group could manipulate supply or price. Similarly, the United States does not produce any nickel, except for a small amount as a by-product of copper and platinum/palladium mining, so we import from the following

[2] A fraction of current supply comes from the stockpile and recycling, but any new supply will be imported.

producers: Canada, 41%; Russia, 16%; Norway, 11%; Australia, 8%; and other, 24% (USGS 2008d). Again, the diversity of producers suggests some security of supply.

The remaining battery materials are all abundant.

6. Conclusions

It is prudent to consider material supply constraints that could be encountered before we embark on an ambitious program of development for any new technology. However, shortages have often been forecast without adequate exploration or consideration of incentives rising prices might provide. Here are some examples (Bratby 2008):

- 1885: The U.S. Geological Survey announces there is "little or no chance" of oil being discovered in California, and a few years later they say the same about Kansas and Texas.
- 1939 and 1949: The Secretary of the Interior says the end of U.S. oil supplies is in sight.
- 1974: The U.S. Geological Survey advises that the United States has only a 10-year supply of natural gas.
- 1972: The Club of Rome warns the world will run out of gold by 1981; mercury and silver by 1985; tin by 1987; and petroleum, copper, lead, and natural gas by 1992.

In the case of materials for lithium-ion batteries, it appears that even an aggressive program of vehicles with electric drive can be supported for decades with known supplies. Of course, larger vehicles with longer ranges require more material, and so heavy reliance on pure electrics could eventually strain supplies of lithium and cobalt. Santini et al. (2009) based on work by Kromer and Heywood (2007), examined the added benefit per-mile-of-range of increasing a vehicle's electric range. There are rapidly diminishing returns to increasing range, which suggests other technologies' use for longer-distance travel. To illustrate, for "full function" vehicle range, it was estimated that a hydrogen fuel cell vehicle, though a loser to conventional vehicles, would be better than an electric vehicle, even though the electric had less range than the hydrogen vehicle.

Further work is required to examine recycling in more detail and to determine how much of which materials could be recovered with current or improved processes. Environmental impacts of both production and recycling processes should be quantified as well. In addition, world demand for these materials in all markets must be projected before concerns about scarcity can be put into proper perspective.

7. Acknowledgments

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Appendix USGS Definitions

Resource — A concentration of naturally occurring solid**,** liquid, or gaseous material in or on the Earth's crust in such form and amount that economic extraction of a commodity from the concentration is currently or potentially feasible.

Reserves — That part of the reserve base which could be economically extracted or produced at the time of determination. The term reserves need not signify that extraction facilities are in place and operative. Reserves include only recoverable materials; thus, terms such as "extractable reserves" and "recoverable reserves" are redundant and are not a part of this classification system.

Reserve Base — That part of an identified resource that meets specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth. The reserve base is the in-place demonstrated (measured plus indicated) resource from which reserves are estimated. It may encompass those parts of the resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics. The reserve base includes those resources that are currently economic (reserves), marginally economic (marginal reserves), and some of those that are currently sub-economic (sub-economic resources). The term "geologic reserve" has been applied by others generally to the reserve-base category, but it also may include the inferred-reserve-base category; it is not a part of this classification system.